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1471 ① cottonseed
② cotton ③ cottonseed industry
④ cottonseed production
⑤ " consumption
⑥ " composition
⑦ " pigments
⑧ " oil
⑨ " proteins
⑩ " grading
⑪ " evaluation
⑫ " cake
⑬ " meal
⑳ cotton " linters
㉑

COTTONSEED AND COTTONSEED PRODUCTS

THEIR CHEMISTRY AND CHEMICAL TECHNOLOGY

Edited by

ALTON E. BAILEY

VOTATOR DIVISION
THE GIRDLER CORPORATION
LOUISVILLE, KENTUCKY

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PREFACE

Among the raw commodities provided by agriculture, cottonseed are almost unique with respect to the diversity of useful products that they supply. For this reason, the compilation of a comprehensive treatise on the chemistry and technology of the cottonseed industry—the objective sought in this volume—has imposed unusual problems.

The most pressing problem, that of bringing expert and authoritative attention to a wide variety of subjects, has been very happily solved by the now-common expedient of enlisting specialists to prepare the individu chapters. However, in following this course, an earnest attempt has been made, through the exercise of rather close editorial supervision and frequent consultation with the authors, to avoid as far as possible the unevenness of viewpoint and execution that is the chief shortcoming of collaborative works.

A second very considerable difficulty has been in deciding how far to extend the scope of the book—in determining how thoroughly to treat the derived products of the cottonseed, and to what extent it might be useful and wise to illuminate the chemistry and the practices of the industry by reference to the related knowledge of nonchemists or engineers. Here, after much thought, a very broad viewpoint was taken. Hence, the utilization, as well as the production of cottonseed products, has been considered in some detail; and attention has been given to such historical, economic, and agronomic factors as have obviously influenced present technological practices in the industry. The editor is fully aware that the inclusion of related data goes somewhat beyond that which is customary in a treatise of this kind. In justification, he would point out that the technical interrelationships between different phases or parts of a complex industry are no less worthy of study than are the details of each part; in his opinion, scientists and technologists are generally in as much need of a good look at the forest as they are of a closer view of the trees.

As a minor consequence of the policy outlined above, it is believed that substantial portions of the text may be recommended to intelligent and interested laymen, as well as to scientific personnel. At least, it is the editor's hope that it may profit a somewhat larger circle of readers than the average volume of science or technology.

In brief, then, this book intends to encompass a broad treatment of the scientific principles underlying a great American industry—an industry which is in fact the child of applied science, for in the beginning cottonseed

was a waste material. It is presented as a text and reference book for students, for workers within the industry, for those engaged in the manufacture or merchandising of products derived wholly or in part from cottonseed, and for scientists and technologists in related fields.

In the task of compiling this volume, the editor and the authors have had the kind assistance of so many different persons that it is impossible to mention the names of all of them here. It must suffice to say that the finished volume represents not only the work of the editor and the twenty-four collaborating authors, but also the contributions of many firms, organizations, and individuals who have furnished illustrations, textual or tabular material, expert criticism and suggestions, or stenographic or clerical assistance. To these collectively, the editor wishes to express his sincerest thanks and appreciation; it is scarcely possible to record his indebtedness to them individually. However, he wishes specifically to acknowledge the invaluable assistance of officials and members of the National Cottonseed Products Association, and particularly of Mr. E. R. Barrow, Chairman of the Technical Advisory Committee of the Association, without whose wise, optimistic, and unfailingly efficient co-operation this volume could by no means have been published.

A. E. Bailey

Louisville, Kentucky
January 9, 1948

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A. HISTORY AND PRESENT STATE OF THE COTTONSEED INDUSTRY

CHAPTER I

HISTORY OF COTTON AND THE UNITED STATES COTTONSEED INDUSTRY

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I. Early History of Cotton and Cottonseed

From earliest days of recorded history down to the present time, the cotton plant has been grown primarily for its fiber. While the seed was for many centuries of little value, it is today one of the more important agricultural commodities of the United States, and the manufacturing of cottonseed and its products constitutes one of the major domestic industries. Cottonseed has, however, never possessed more than a fraction of the value of the fiber. Consequently, the production of seed—which obviously varies directly with lint production—is not only closely related to, but is dominated by, the factors determining the production of lint cotton. It is, therefore, appropriate that attention be given to lint in any study of the history of cottonseed.

A. Early Use of Lint Cotton

It is not known when man first began to use lint cotton for clothing or cottonseed for feed, food, fertilizer, or other purposes. Archaeological evidence, discovered in the 1920's, indicates that as early as about 3000 B.C. cotton was being used in India to make fabric and string. Remnants of cotton material dating back that far were unearthed by members of the Archaeological Survey of India at Mohenjodaro, about 200 miles northeast of Karachi in the Sind province of India. A careful analysis of these remnants—one small piece of cloth and two short pieces of string—conducted in the Technological Laboratory of the Indian Central Cotton Committee showed conclusively that they were made of cotton. The fabric was described as corresponding in weight to a cloth of about 2 ounces per square yard, made of yarns of about 34's count and with the equivalent of about 60 ends and 20 picks per inch. The preservation of this piece of cloth was attributed to the formation of silver salts from the silver vase

to which the material was found adhering. Both pieces of string were reported to have been "twenty-four-fold cotton" cords, the count of a single strand being 14's in one and 18's in the other.[1]

Cotton mummy cloths have been found in Peru but the date of their origin is undetermined. Egyptian mummy cloths, said to date back to 5500 B.C. or earlier, were long considered by many to have been made of cotton.[1] But in 1834 James Thomson reported that he and an eminent microscopist named Bauer examined a large variety of such cloths and found them all to be linen.[1, 2] Handy [3] points out, however, that even if all the Egyptian mummy cloths were made of linen this would not necessarily prove that the Egyptians of that day did not use cotton. Baines,[4] on the other hand, indicates that linen was ". . . almost the only kind of clothing used in Egypt till after the Christian era." In 1928 the Bolton Museum of England is reported to have received some specimens of fabric from Middle Egypt ". . . believed to belong to the civilization existing in the Nile Valley [5] about 12,000 B.C." But this fabric is apparently also linen.[1]

The earliest authenticated date of the specific reference to cotton in recorded literature seems to be about 800 B.C. Cotton is referred to in the Hindoo Rig Veda hymn which is considered by some to date back to around 1500 B.C.,[6] but A. B. Keith (in *Religion and Philosophy of the Verda and Upanishads,* 1925, Volume I, Chapter 1) reports that it is not possible to assign any exact date to the Rig Veda, except that it is not later than 800 B.C.[1] Handy [3] also points out that cotton is referred to in the *Digest of Ancient Laws* ascribed to Manu, about 800 B.C., in such a way as to indicate that its production and manufacture must have been known for generations.

Many historical references indicate that cotton was manufactured by the Hindus in early times in sufficient quantities to meet their own needs and to sell to traders from other places.[6] Herodotus, writing in about 445 B.C., indicated that cotton was the customary wear of the Indians and that this "tree wool" exceeded the wool of sheep both in "beauty and goodness." [4] Other references cited by both Handy [3] and Baines [4] suggest that India was the center of cotton manufacturing from the time of the earliest recorded references down to possibly the fifteenth century A.D. However, the manufacture of cotton goods appears to have been common in the early days of the Christian era in many countries of the near East,

[1] A. N. Gulati and A. J. Turner, *A Note on the Early History of Cotton,* Indian Central Cotton Committee, Bombay, Bulletin No. 17, 1928, pp. 1–5.

[2] E. Baines, *History of the Cotton Manufacture in Great Britain,* Fisher, Fisher, and Jackson, London, 1835, pp. 533–536.

[3] R. B. Handy, in "The Cotton Plant," *U.S. Dept. Agr. Expt. Sta. Bull.,* **33,** 17–25, 1896.

[4] E. Baines, *History of the Cotton Manufacture in Great Britain,* Fisher, Fisher, and Jackson, London, 1835, pp. 16–17.

[5] *Textile Weekly:* **1,** No. 20, 572 (July 20, 1928).

[6] J. A. B. Scherer, *Cotton as a World Power,* Stokes, New York, 1916, pp. 16–23.

in Egypt, and in Italy. Since the time of Herodotus, references to cotton production and manufacture have appeared in innumerable places.

B. Early Crushing of Cottonseed

The first record of the crushing of cottonseed to obtain oil or cake apparently dates back to the early Hindu writings. Old medical books of the Hindus are said to have recommended cottonseed oil for external applications and to have described the method of extracting the oil as consisting mainly of first pounding the seed and then boiling the pounded contents.[7]

It has been said that at an early stage of history the Chinese were not only producing oil, but were using methods in the crushing of oilseed somewhat similar to those of oil mills of modern times. The seed was crushed and reduced to meal under an edgestone, the meal heated in an open pan, and the oil pressed out by a wedge press, the wedges being driven by hammers.[8] The seed being crushed at that early date, however, was not necessarily cottonseed.

J. W. Allison, past President of the Interstate Cotton Seed Crushers' Association; wrote in 1910 of having been in Asia where cottonseed oil was used many centuries earlier. In a small pamphlet which he published without a title Mr. Allison stated: "It is not improbable that cottonseed oil as a food and cottonseed cake as a feed in some crude form was known to that all-wise people, the Chinese, many hundreds of years ago, and I have, myself, with emotions of mixed awe and amusement, watched in Trans-Caspian Asia the slow and laborious operations of cottonseed oil mills, whose products from the same spot, had in years ago, it is claimed, fed the armies of that great Alexander of Macedon when he had marched eastward to fulfill his dream of world conquest."

The modern pressing equipment used to extract oil from cottonseed and similar materials represents great improvement over the wedge press. Wedge pressing was followed by the use of the screw press. Then came the Dutch or stamper press invented in Holland in the seventeenth century, which was used in Europe for many years in crushing cottonseed grown in Egypt. And finally in April, 1795, Joseph Bromah obtained a patent in England for a hydraulic press, which even at that early date could be easily constructed and had almost unlimited power.[8a]

[7] Y. G. Pandit, *Report of the Oil Processing Industry of the Bombay Presidency,* Indian Government Central Press, Bombay, 1914, p. 22.

[8] *Encyclopedia Britannica,* 14th ed., Vol. 16, 1939, p. 749.

[8a] L. W. Bass and H. S. Olcott, *Ind. Eng. Chem., News Ed.,* **18,** 139–142 (1940).

II. Important Developments since 1700 in Production and Consumption of Lint Cotton

The quantity of lint cotton (and cottonseed) produced and consumed in the world prior to the eighteenth century was relatively small. It has been estimated by Hammond [9] that in 1790 the world production of cotton lint was equivalent to a little under 1 million bales (of 478 pounds), most of which was grown in India and the West Indies. This, however, undoubtedly represented a tremendous increase over the quantity produced and consumed in the early 1700's. In Great Britain (for which import statistics are available back to 1697) annual imports of raw cotton in the first quarter of the 1700's were only about 2 to 6% as large as in 1790. And the imports in 1790 were only 56% as large as in 1800. The eighteenth century, therefore, appears to have been a period in which there was a rather rapid increase in total world production and consumption of lint cotton and in the production of cottonseed. The absolute increase in lint production for the eighteenth century, nevertheless, was exceeded many-fold during the nineteenth century. The tremendous increase in lint cotton production and consumption during the eighteenth and nineteenth centuries, and especially in the last half of the 1700's and throughout the 1800's, was due in a large measure to a number of inventions, most of which occurred during the eighteenth century.

A. Improvements in Spinning and Weaving

Prior to the middle of the eighteenth century, cotton spinning and weaving and, for the most part, other operations of textile production, were largely carried on by hand in the workers' homes. The spinning wheel and the hand loom were about the same as they had been for centuries. The operations employed in the making of cloth at that time were not fundamentally different from those of today. Then as now, the raw fiber passed through the processes of cleaning, carding, drawing, spinning, weaving, and finishing. The equipment used and the methods employed in these operations, however, were very different. The cotton or other fiber was first cleaned, whenever this was required, and then laid on a hand brush called a "card" measuring some 12 inches by 5 inches. By "combing" the cotton over and over between two of these cards, most of the fibers were brought into more or less parallel positions. The cotton was then stripped off the card as a fleecy roll and was ready for the spinning process. The spinner, by turning the spinning wheel—thereby making the spindle revolve—while at the same time drawing out the "cardings," converted the latter into long, thick, loose rolls called "rovings." In a further similar

[9] H. Hammond, in "The Cotton Plant," *U.S. Dept. Agr. Expt. Sta. Bull.*, **33**, 42 (1896).

process these rovings were twisted and drawn into yarns which were longer, tighter, stronger, and finer than the rovings.

In the process of weaving by hand loom as practiced at that time, the shuttle carrying the "weft yarn" (which runs across the fabric) was passed from one side of the cloth to the other by hand. Despite the primitive state of the weaving process, it is said that one weaver could keep six or eight spinners busy providing him with sufficient yarn.[10]

During the last three quarters of the eighteenth century, however, marked changes occurred in the design of both spinning and weaving equipment. The great inventions in textile machinery, and the rate at which they were put into use, were related to important developments in communication and transportation, iron smelting, and steam power. These developments acting and reacting upon each other brought about marked changes in the textile industries of England and other countries, and in industry in general. The changes were so great and so rapid that they are generally referred to as "revolutionary."

The first of the important inventions relating to textiles came in 1732 or 1733 when a French refugee in England, named Lewis Paul, working with John Wyatt, a carpenter, developed an improved method of spinning sometimes referred to as "roller spinning" or "spinning by rollers." This process, which provided for the yarns being twisted or spun to pass between revolving rollers, was patented in 1738 in Paul's name. However, Baines,[11] who made a study of the situation in the early 1830's, claims that Wyatt was really the inventor and also that this was the machine later ascribed to and patented by Sir Richard Arkwright in 1769.

Between 1733 and 1738, and at approximately the same time the system of "roller spinning" was being worked out by Wyatt and Paul, John Kay invented a mechanical shuttle which became generally known as the "flying shuttle." This development greatly increased the speed of weaving and made it practicable to produce much wider cloth. Consequently, there was an increase in the number of spinners required to provide sufficient yarn to keep a weaver fully employed and this created still greater need for improved methods of spinning.[10]

At the time Kay's flying shuttle was being introduced, others were at work trying to devise speedier methods of producing yarn. In 1748 Daniel Bourn and Paul of England each took out patents on machines for "carding," an essential process preparatory to spinning, which at that time required a great deal of labor.[10] It is said that, while Paul's machine for "carding by cylinders" represented a great improvement, it was not known

[10] L. S. Wood and A. Wilmore, *The Romance of the Cotton Industry in England,* Oxford Univ. Press, London, 1927, pp. 76–82.

[11] E. Baines, *History of the Cotton Manufacture in Great Britain,* Fisher, Fisher, and Jackson, London, 1835, pp. 119–124.

in Lancashire for twelve years nor put into general use for more than twenty years.[12]

In 1770, after possibly five or six years of work, James Hargreaves patented what he called the "spinning jenny," this device being named in honor of the inventor's wife. The first spinning jenny made by Hargreaves was said to have had 8 spindles on 1 frame, turned by the same wheel. But this number had been doubled by the time he took out his patent in 1770 and it was later increased to 20, then 30, and eventually to 120. Despite Hargreaves' attempt to keep his machine a secret, his house was attacked in 1768 and the machine he was working on destroyed.[10] This, and similar experiences by other inventors of that period, grew out of the fear of workers in the industry as to what such machines would do to their future employment and welfare.

At the time that Hargreaves was developing his machine, Arkwright was working on a mechanical spinning frame with John Kay. By 1769 a practical machine had been developed and patented. This machine is said to have produced yarns which were stronger, more even in thickness, and more regular in twist than those from Hargreaves' machine. The yarn produced on the spinning jenny was only strong enough for the weft, whereas the new machine of Arkwright's could spin threads strong enough for the warp. It also possessed other important advantages. Shortly thereafter, Arkwright began working on other processes and is said to have made some additional contributions, including the invention of a machine [10] which combined drawing, roving, and spinning "all in one set."

Meanwhile, Samuel Crompton, who had been a weaver for some time, worked at night on a machine involving a combination of certain of the principles of both Hargreaves' "jenny" and Arkwright's "frame." The machine was completed about 1779 and became generally known as a "mule." Baines [13] described it as having spindles without bobbins (like the jenny) to give the twist, and a system of rollers (like the frame) to reduce the roving. But the spindles, instead of being stationary as on the other machines, were erected on a movable carriage. This permitted the spindles to move away from the drawing rollers as the threads were being twisted and to move back as the thread or yarn was wound on the spindles.

As a result of the inventions of Hargreaves, Arkwright, and Crompton, potentialities in yarn production had been increased many-fold. Consequently, with the use of the improved spinning equipment, a given number of workers could produce many times more yarn than an equal number of workers could weave. Thus, the situation was then the reverse of that existing in the 1730's. It is related that Dr. Edmund Cartwright, a clergy-

[12] E. Baines. *History of the Cotton Manufacture in Great Britain*, Fisher, Fisher, and Jackson, London, 1835, pp. 172–174.

[13] E. Baines, *History of the Cotton Manufacture in Great Britain*, Fisher, Fisher, and Jackson, London, 1835, pp. 197–199.

man, became interested in this situation while talking with some merchants in 1784. After visiting a cotton mill he began working on a new loom, which was patented in 1785. After four more years, Cartwright had improved his machine which first was operated by a bull. He set up a factory at Doncaster and operated his machine with a steam engine, the latter having been invented twenty years earlier. By about 1815, after some improvements made by others, the power loom had apparently come into fairly general use in Lancashire, thereby greatly reducing the labor requirements for weaving.[14]

These and other inventions relating to cotton spinning and weaving, together with the development of steam power, improved transportation and communication, and other technological developments, greatly increased the demand for raw cotton, especially in Great Britain. For a long time the hand spinners and hand weavers attempted to prevent the development of improved machinery. Also, from 1736 to 1774 there was a British law prohibiting the sale and use of cloth containing cotton except in the weft. Nevertheless, there was a remarkable increase in the consumption of cotton in England during the last half of the eighteenth century and the early part of the nineteenth century. Marked increase in consumption also occurred in the United States and in Continental Europe.

Although efforts were made by the British Government to prevent the improved spinning and weaving machinery developed in that country from becoming accessible to other parts of the world, it is said that, ". . . as early as 1775 a spinning jenny of 24 threads was put in operation by a joint stock company [15] at Philadelphia." Fifteen years later Samuel Slater, who had worked in the Arkwright factory in England, entered into a contract with Moses Brown of Providence, Rhode Island, to build a complete spinning mill. This mill, powered by a waterfall on the Pawtucket River, was a success from the start. The waterframe built by Slater was patented in 1791 and other improvements in the machinery in use in this country followed shortly thereafter.[16]

B. Development of the Saw Gin

The above-mentioned British inventions contributed to an expansion in the production and consumption of lint cotton and cottonseed largely through their stimulus to the demand for cotton. Late in the eighteenth century an invention occurred in the United States which had a most important effect on the expansion of cotton production and consumption

[14] L. S. Wood and A. Wilmore, *The Romance of the Cotton Industry in England,* Oxford Univ. Press, London, 1927, pp. 89–90.

[15] D. C. Roper, "Supply and Distribution of Cotton," *Bureau of the Census Bull.,* **97,** 33 (1908).

[16] K. Coman, *Industrial History of the United States,* Macmillan, New York, 1920, pp. 152–153.

through its influence on the supply of cotton. This was the invention of the gin by Eli Whitney in 1793.

Prior to the development of the gin, one of the most important factors preventing the rapid increase in cotton production in the United States was the large amount of hand labor required to separate the lint from the seed. The scarcity of labor in the new country for planting, cultivating, and harvesting was also an important factor retarding production, but much less important than the problem of separating lint from seed. Cotton gins of one type or another apparently had been in use, at least on a limited basis, for centuries. But Whitney's gin is generally considered one of the most important of all technological developments relating to cotton.

As far back as about 300 B.C. a crude type of gin originated in India employing rollers which, when rotated close together, would pull the lint back between the rollers and leave the seed behind.[17] The general principles of this gin were the same as those of the modern roller gin used in ginning Egyptian, American Egyptian, Sea Island, and some types of Peruvian and Brazilian cottons. These cottons and apparently most of the early Eastern cottons possessed characteristics which made the separation of the lint from the seed much easier than is the case for the so-called Upland varieties.

In the early colonial days the colonists living along the seaboard and on adjacent islands apparently first grew Sea Island varieties. One of the first cotton gins of any kind in the United States was apparently owned by Mr. Dubreuil of Louisiana, but one introduced from the Bahama Islands about 1790 by Dr. Joseph Eve of Augusta, Georgia, is said to have been more practical.[17] As more and more of the population of the country moved inland, it was apparently found that the Upland varieties were much better adapted to local conditions than the Sea Island varieties. This, along with the increasing demand for lint cotton and the increasing supply of labor (through immigration, importation of slaves, etc.), created a great need for some mechanical aid for separating the lint of the Upland varieties from the seed. It has been said that the crude roller gins then in use made it possible for a worker to separate about five times as much Sea Island cotton per day as could be separated by hand.[17] In addition, the great reductions which had been made in the labor required to spin and weave lint cotton no doubt stimulated interest in the possibilities of developing an even more suitable machine. In the spring of 1793, Eli Whitney, a graduate of Yale who went south to take a job as tutor, but who failed to complete his arrangements for teaching, became interested in the problem.

Tompkins [17] reported that Whitney, who was living in the home of

[17] D. A. Tompkins, *Cotton and Cotton Oil*, published by the author, Charlotte, N. C., 1901, pp. 2–26.

Mrs. Nathaniel Greene, widow of a Revolutionary General, was provided with a room in the basement of Mrs. Greene's house in which to conduct his experiments. Apparently, within a few weeks after beginning his experiments, Whitney had developed a small hand-operated machine, which worked successfully. On June 20, 1793, he filed a petition for a patent with Thomas Jefferson, Secretary of State. On March 14, 1794, the patent was issued to Whitney, "signed by George Washington, President, Edmund Randolph, Secretary of State, and Wm. Bradford, Attorney General."

Twenty-seven suits for infringement of the gin patent are said to have been brought before the United States Court, District of Georgia.[17] This was apparently due in part to the simplicity of the Original Whitney machine, which made it easy to construct, and to the fact that the original petition and accompanying illustrations were destroyed by fires in 1836. Also, the patent issued to Whitney indicated that his original gin used wire rather than saws for the so-called "teeth." On May 12, 1796, Hogden Holmes of Augusta, Georgia, obtained a patent for a gin similar to that of Whitney. The Holmes' machine seems to have been the first in which saws were used. Seabrook, President of the Agricultural Society of South Carolina, in a book published in 1844 is quoted by Tompkins as follows: "The Holmes machine was set up in the grist mill of Captain James Kincaid on Mill Creek in Craven (now Fairfield) County, South Carolina, in 1795, and is reported to have been the first of the saw gins used in that State." Regarding this gin Tompkins wrote: "The first power saw gin, which is to say the first real practical and productive gin in the world, was made by Holmes and was run by water power . . . in 1795."

From this time, until after the abolition of slavery, a great deal of the cotton produced was grown on plantations which had their own gins. It has been said that in the years immediately following Whitney's invention a good many crude gins were made in blacksmiths' shops on the plantations.[17] While there are no statistics on the number of gins in use in the late 1790's or in a large part of the eighteenth century, the very sharp increase in cotton production is adequate evidence of the rapid expansion in the ginning facilities available to cotton producers throughout the Cotton Belt.

C. Expansion in Cotton Production and Consumption

Very few data are available on cotton production and consumption during the eighteenth century. Data are available, however, showing imports of raw cotton into Great Britain for selected years from 1697 to 1764 and annually from 1781 to date (Table 1). Estimates of cotton production and consumption in the principal foreign cotton-producing and -consuming countries or groups of countries at approximately ten-year

TABLE 1

Imports of Cotton into the United Kingdom and Imports from United States as Percentage of Total Imports in Specified Calendar Years from 1697 to 1945[a] (in terms of 478-lb. net bales)

Year	Imports, 1000 bales	Year	Imports, 1000 bales	Year	Imports, 1000 bales	Per cent imports from U.S. were of total imports	Year	Imports, 1000 bales	Per cent imports from U.S. were of total imports	Year	Imports, 1000 bales	Per cent imports from U.S. were of total imports
1697	4.1	1790	65.8	1810	277.2	—	1830	552.2	70.30	1850	1388.2	74.32
1701	4.2	1791	60.1	1811	191.6	—	1831	603.9	—	1851	1584.5	78.78
1700–05 *av.*	2.5	1792	73.0	1812	131.9	—	1832	600.1	—	1852	1945.2	82.35
1710	1.5	1793	39.8	1813	106.6	—	1833	635.3	—	1853	1873.0	73.55
1720	4.1	1794	51.0	1814	125.6	—	1834	683.8	—	1854	1856.3	81.38
1730	3.2	1795	55.2	1815	207.8	—	1835	760.9	78.21	1855	1865.6	76.44
1741	3.4	1796	67.2	1816	196.5	—	1836	851.4	—	1856	2142.0	76.18
1751	6.2	1797	48.9	1817	261.3	—	1837	852.1	—	1857	2027.9	67.55
1764	8.1	1798	66.7	1818	370.9	—	1838	1062.4	—	1858	2163.9	80.56
1771–75 *av.*	10.0	1799	90.8	1819	313.3	—	1839	814.6	—	1859	2564.8	78.44
1776–85 *av.*	14.2	1800	117.2	1820	317.3	59.34	1840	1239.5	82.34	1860	2909.9	80.23
1781	10.9	1801	117.2	1821	277.3	70.52	1841	1020.9	73.41	1861	2629.7	65.20
1782	24.7	1802	126.2	1822	298.8	70.73	1842	—	—	1862	1096.2	2.58
1783	20.4	1803	112.6	1823	400.4	74.47	1843	1408.4	85.56	1863	1401.8	0.95
1784	24.0	1804	129.4	1824	312.5	61.71	1844	1351.7	80.55	1864	1870.5	1.59
1785	38.5	1805	124.9	1825	477.0	61.36	1845	1510.4	86.80	1865	2047.1	12.88
1786	40.7	1806	121.7	1826	371.6	73.68	1846	978.8	85.91	1866	2881.8	37.75
1787	48.6	1807	156.7	1827	570.0	79.62	1847	773.7	70.91	1867	2642.0	41.82
1788	42.8	1808	91.2	1828	476.5	66.63	1848	1092.7	79.00	1868	2779.8	43.23
1789	68.2	1809	194.2	1829	466.0	70.56	1849	1580.5	83.99	1869	2555.6	37.44

TABLE 1 (*concluded*)

Year	Imports, 1000 bales	Per cent imports from U.S. were of total imports	Year	Imports, 1000 bales	Per cent imports from U.S. were of total imports	Year	Imports, 1000 bales	Per cent imports from U.S. were of total imports	Year	Imports, 1000 bales	Per cent imports from U.S. were of total imports
1870	2802.0	53.48	1890	3752.1	73.42	1910	4127.1	74.52	1930	2537.7	48.74
1871	3720.0	58.41	1891	4173.4	81.08	1911	4617.3	76.23	1931	2281.6	40.62
1872	2947.4	44.41	1892	3713.9	79.17	1912	5869.9	77.16	1932	2630.9	58.13
1873	3195.8	54.50	1893	2964.0	74.52	1913	4548.7	72.89	1933	2939.1	53.88
1874	3278.0	55.84	1894	3740.8	77.91	1914	3899.9	68.90	1934	2641.4	36.30
1875	3122.1	56.38	1895	3675.8	79.38	1915	5538.9	76.39	1935	2661.2	44.98
1876	3112.7	62.69	1896	3671.3	79.44	1916	4541.8	75.86	1936	3234.7	39.97
1877	2835.3	67.31	1897	3607.0	80.05	1917	3395.8	73.08	1937	3473.0	46.10
1878	2804.1	76.56	1898	4453.0	84.82	1918	3115.2	65.55	1938	2524.7	36.77
1879	3074.0	73.67	1899	3402.2	75.88	1919	4096.8	70.00	1939	2677.8	37.99
1880	3407.2	75.17	1900	3682.4	77.57	1920	3969.1	73.28	1940	2966.9	49.53
1881	3512.7	72.12	1901	3827.8	80.93	1921	2453.0	68.31	1941	1706.5	36.99
1882	3732.5	64.72	1902	3800.7	75.07	1922	2995.8	63.76	1942	2464.4	28.33
1883	2628.3	71.46	1903	3751.3	75.91	1923	2702.7	51.79	1943	2065.9	56.83
1884	3659.4	69.27	1904	4089.8	76.26	1924	3300.5	60.17	1944	1688.7	27.97
1885	2949.0	73.65	1905	4610.0	78.70	1925	3962.7	64.71	1945	1867.8[b]	26.45[b]
1886	3588.0	75.36	1906	4199.5	74.15	1926	3640.8	61.46	—	—	—
1887	3726.3	70.24	1907	4993.5	73.56	1927	3239.2	59.33	—	—	—
1888	3622.8	77.88	1908	4311.1	77.08	1928	3153.9	57.58	—	—	—
1889	4053.3	73.49	1909	4579.0	74.95	1929	3221.3	54.31	—	—	—

[a] Data for 1697 through 1887 from *Quarterly Reports of the Bureau of Statistics*, U.S. Treasury Dept.; 1888–1908 from *Statistical Abstract of the United Kingdom;* 1909 to date from *Trade of the United Kingdom.* Linters were not separately reported prior to 1920; if any were imported prior to that date they probably would be included here; data for 1920 and later years exclude linters. Imports from the United States from which percentage relation was worked out for 1820–1833 were from E. Baines, *History of Cotton Manufactures in Great Britain*, 1835.

[b] Preliminary report.

intervals for the period from 1790 to 1890 were published in graphic form by Hammond [9] in 1896, and are still about the only such estimates extending that far back. Estimates of the United States' production are available annually from 1790 to date, while annual estimates of domestic cotton consumption begin in 1826–27, with scattered estimates for six earlier years, the earliest being 1799–1800. These data when considered in comparison with the time of the great inventions reviewed above give further indication of the importance of the improvements made in cotton spinning, weaving, and ginning in relation to the expansion of cotton production and consumption.

These improvements, together with cheaper and faster transportation and communication, were no doubt largely responsible for the rapid expansion in lint cotton production and consumption during the seventeenth and eighteenth centuries. However, they were not the only important contributing factors. The increasing population throughout the world augmented both the need for cotton and other textiles and the supply of labor for producing and manufacturing these products. Certain technological improvements in textile printing, including the establishment of the first print works in Lancashire in 1764 and the successful application of roller printing by Bell in 1785,[18] also contributed to the expansion. Just as the improvements in spinning and weaving reduced the costs and widened the market for gray goods, this invention did the same for finished goods. Still other factors included the installation of labor-saving machinery in other industries, increasing wages, and increasing international trade—all of which affected the general level of purchasing power of consumers and of nations. But, whatever the causes, it is interesting to note the extent of some of the increases in lint cotton production and consumption since 1700, remembering that changes in the production of cotton lint were accompanied by corresponding changes in the production of cottonseed.

In 1720 imports of lint cotton into the United Kingdom were equivalent to about 4,127 bales (of 478 pounds), about the same as at the turn of the century; however, imports dropped to below 3,440 bales in 1730 and 1741. Thus, for this period of four decades there was a substantial net decline. On the other hand, from 1741 to 1782, also four decades, there was a seven-fold increase, and in the last eighteen years of the century the increase was nearly five-fold. From 1764 to 1800 gross imports increased from 8,000 to 117,000 bales (see Table 1). The absolute increase in the last three and one-half decades of the century was 26 times as great as the increase in the first six and one-half decades. It was only during the last two and one-half to three decades of the century that relatively large-size

[18] E. Baines, *History of the Cotton Manufacture in Great Britain*, Fisher, Fisher, and Jackson, London, 1835, pp. 262–265.

machinery for carding, drawing, roving, and spinning was erected in units or sets for operation by water or steam power.

During the first decade of the nineteenth century the absolute increase in the total imports of cotton in the United Kingdom was as great as during the entire eighteenth century.[19] By 1860, just before the American Civil War, total British imports reached 2.9 million bales, a twenty-five-fold increase over those of 1800. With only negligible imports from the United States from 1862 to 1864, the total dropped to between 1 and 1.9 million bales. By 1866 total British takings were almost back to the pre-war peak, and in 1871 they exceeded 3.7 million bales. After that the upward trend flattened off considerably for about three decades.

In 1912 total imports of cotton into the United Kingdom reached an all-time high of almost 5.9 million bales, 77% of which represented American cotton. But since that time there has been a rather marked downward trend in the quantity of cotton taken by British mills, due in a large measure to reduced exports of cotton textiles. The latter in turn resulted from increased cotton textile production in Japan, India, Brazil, and in numerous less important countries which, like India and Brazil, formerly purchased sizeable quantities of British goods.

Cotton consumption as well as cotton production was comparatively small in the United States prior to 1790. In that year, the first for which production estimates are available, domestic production and consumption amounted to only a few thousand equivalent 478-pound bales. Soon after this date, however, tremendous increases took place, especially in production.

The growth in cotton manufacturing in the United States following the establishment of the successful mill at Pawtucket in 1790 was quite rapid, even though fourteen years later (in 1804) it is said that there were only 4 mills in successful operation. However, by 1811 there were 87 mills operating 80,000 spindles.[20] Twenty years later the number of cotton manufacturing "establishments" totaled 801, in which 62,208 wage earners were employed—the quantity of cotton consumed exceeding 150,000 bales (see Table 2). In 1839 there were 1,240 establishments in the United States, the largest number shown in any of the following six decennial census returns. The quantity of cotton consumed by mills in the United States nevertheless continued to increase, and by 1879 exceeded 1.5 million bales, a ten-fold increase over consumption in 1831 despite the setback during the Civil War. During the last ten years of the nineteenth century domestic

[19] It should be noted that for the comparatively few years for which figures on re-exports of cotton from the United Kingdom are available the quantity of cotton retained for use in that country was generally some 85 to 90% of the total imports.

[20] K. Coman, *Industrial History of the United States,* Macmillan, New York, 1920, p. 184.

cotton consumption ranged between 2.3 and 3.7 million bales annually and for the first time appears to have exceeded that of the United Kingdom.

Throughout the 1800's United States cotton production was seldom less than two and one-half to three times as large as domestic consumption and in many years of the first half of the century it was five to eight times as large. Large exports from this country went to Continental Europe as

TABLE 2

Manufactures of Cotton: Number of Establishments, Number of Wage Earners, Value of Products, and Total Cotton Consumption in the United States in Specified Years, 1831–1939[a]

Year	Establishments, number	Wage earners, number		Quantity of cotton consumed, bales[b]		Value of products	
		Total	Average per mill	Total[c]	Average per mill	Total, 1000 dollars	Average per mill, dollars
1831	801	62,208	77	154,915[d]	193	—	—
1839	1240	72,119	58	236,525[d]	191	46,350	37,379
1849	1094	92,286	84	575,506[d]	526	61,869	56,553
1859	1091	122,028	112	845,410[d]	775	115,682	106,033
1869	956	135,369	142	796,616[d]	833	177,490	185,659
1879	756	172,544	228	1,570,344	2077	192,090	254,087
1889	905	218,876	242	2,518,409	2783	267,982	295,819
1899	1055	302,861	287	3,873,165	3671	339,200	321,517
1904	1154	315,874	274	4,278,980	3708	450,468	390,354
1909	1324	378,880	286	4,621,742	3491	628,392	474,616
1914	1287	385,964	300	5,597,362	4349	688,094	534,650
1919	1452	440,362	303	6,419,734	4421	2,166,169	1,491,852
1921	1490	419,421	281	5,909,820	3966	1,304,282	875,357
1923	1603	487,890	304	5,680,554	3544	1,974,350	1,231,659
1925	1596	461,346	289	6,455,852	4045	1,789,043	1,120,954
1927	1567	482,554	308	6,834,063	4361	1,632,221	1,041,622
1929	1483	440,197	297	6,105,840	4117	1,589,347	1,071,711
1931	1314	342,788	261	4,866,016	3703	847,783	645,193
1933	1229	392,682	320	5,700,253	4638	900,060	732,352
1935	1212	382,528	316	6,351,160	5240	1,028,166	848,322
1937	1272	346,016	272	5,747,978	4519	1,340,646	1,053,967
1939	1248	312,249	250	7,783,774	6237	1,168,171	936,034

[a] Compiled from the Decennial and Biennial Reports of the Bureau of the Census except "cotton consumption" which is from *Cotton Production and Distribution*, and except for 1831 which is from *U.S. Dept. Agr. Expt. Sta. Bull.*, **33** (1896). Generally the data include manufactures of broad woven cotton goods, narrow fabrics, yarn and thread, but exclude "lace goods," which prior to 1910 were included in the "millinery" category. The series are not strictly comparable over the century owing to changes in classification of data requested in the various Schedules of the Bureau of the Census. This is due largely to changes in the definitions of a "cotton manufacturing establishment" arising out of changes in (*a*) the percentage of cotton in relation to other fiber content of the product, (*b*) the value of the products, (*c*) the number of plants comprising "an establishment," and (*d*) the inclusion in the value of products in 1939 of products of the "dyeing and finishing departments of cotton weaving mills," which were formerly included in the "dyeing and finishing" industry.

[b] American in running bales, counting round bales as half bales, and foreign in bales of 500 pounds except as noted.

[c] Cotton mills included only in 1879 and subsequent years; figures for 1904 and subsequent years do not include foreign cotton.

[d] Equivalent 500-pound bales.

well as to the United Kingdom. Just before the Civil War (1859) domestic production reached 4.3 million bales with exports totaling about 3.5 million bales. By 1898 production had reached a new high of 11.4 million bales. The record high exports for the nineteenth century occurred in 1897–98 at 7.8 million bales.

Production, consumption, and exports of the United States since the beginning of the twentieth century are familiar to most of those interested in the domestic cottonseed crushing industry. Furthermore, such information is readily available from any number of sources.

Hammond's [9] estimates, previously referred to, give at least a rough indication of cotton production and consumption for approximately ten-year intervals from 1790 to 1890 for some of the major foreign countries. These estimates indicate a marked upward trend in production in the British East Indies and in the Mediterranean area (mainly Egypt) during the nineteenth century. In the West Indies there was a downward trend, while in Brazil production showed little variation, upward or downward.

Estimates of consumption from the above source indicate an upward trend in cotton consumption on the continent of Europe, which for the nineteenth century as a whole was somewhat greater than the increase which occurred in Great Britain. However, during the first half of the 1800's the increase for the continent was considerably smaller than that for Great Britain, and was more comparable with that which occurred in the United States. The estimated consumption in India increased only about 100,000 bales between 1800 and 1871—from approximately 400,000 to 500,000 bales. By 1890, however, it had increased to well above 1 million bales.

Except possibly for the United States and the United Kingdom the above estimates of lint production and consumption are probably extremely rough approximations. Nevertheless, they give an indication of some of the tremendous changes which occurred in one of the most important phases of cotton's long history.

III. History and Growth of Cottonseed Crushing in the United States

A. Early Inventions and Developments in the Domestic Industry

It is a historical fact that cottonseed has been used, at least to some extent, for producing oil for many centuries. But there are still many countries where relatively small proportions of the cottonseed produced are crushed. Even in the United States much of the cottonseed produced was unused until the latter part of the nineteenth century. Since that time,

however, practically all the cottonseed produced in the United States has been used for some purpose.

One of the earliest, if not the earliest, recorded experiments relating to the use of cottonseed for the production of oil in the United States was carried out in 1768. At that time Dr. Otto, a Moravian of Bethlehem, Pennsylvania, made some experiments in the extraction of oil. On September 20, 1768, he presented to the American Philosophical Society of Philadelphia samples of cottonseed oil together with a statement that 1.5 bushels of cottonseed yielded 9 pints of oil.[21] Fifteen years later the possible importance of cottonseed as a source of both oil and cattle feed received considerable recognition in London; this may have had some influence on subsequent developments in the United States. In that year certain tests were made on cottonseed in the presence of the Secretary of the London Society of Arts and, as a result, that organization offered gold and silver medals to the planter of the West Indies who would extract a ton of oil from cottonseed and make "hard and dry cakes" as food for cattle.[22] Although there is apparently no account of any medals having been awarded, this may have been a factor in stimulating interest in cottonseed products. A somewhat similar offer is said to have been made by the South Carolina Agricultural Society in 1785.[23]

Prior to the invention of the cotton gin in 1793, the production of cotton and cottonseed in the United States was quite small. Consequently, there was no particular problem of disposing of the seed and no great over-all loss involved in failure to use that portion of the seed not required for planting. This became less and less the case, however, as cotton production in the United States began to increase rapidly. With cottonseed production amounting in volume to about twice that of cotton lint, the importance of being able to utilize this product became more evident and began receiving more and more attention.

On March 2, 1799, a Mr. C. Whiting was granted a patent [21] for "a process for extracting oil from cottonseed." Apparently all records relating to this patent have been destroyed. Consequently, nothing is known regarding the process or whether it was ever put into operation. Some observers have thought, however, that it could well have been a patent for a "cotton screw press." This surmise resulted from the report (when Mississippi was still a territory of the British Dominion) of a planter of Natchez, by the name of Sir William Dunbar, who, in ordering such a press from Philadelphia in 1801, wrote his correspondent that he expected to use it in making cottonseed oil.[21] There is no record that Dunbar ever made any practical use of any knowledge he had of cottonseed crushing, although it

[21] *Encyclopedia Americana,* 1932 ed., Vol. 8, pp. 85–87.
[22] L. L. Lamborn, *Cottonseed Products,* Van Nostrand, New York, 1920, pp. 17–20.
[23] H. C. Nixon, "The Rise of the American Cottonseed Oil Industry," *J. Political Economy,* **38,** No. 1 (Feb., 1930).

may be more than just a coincidence that more than thirty years later Natchez was one of the first places where the commercial manufacture of cottonseed oil was attempted.

It is reported that in 1802 Benjamin Waring of Columbia, South Carolina, was operating an oil mill in which he crushed flaxseed, sesame seed, and some cottonseed. Another reference to Waring's mill appears in 1826.[24] According to a statement appearing in the *Niles Register* of 1829 from which an extract was made by a New Orleans newspaper and republished in the *Oil, Paint and Drug Reporter,* Dr. George Hunter, chemist and druggist of Philadelphia, after having made some experiments with cottonseed oil, became quite interested in the possibilities of producing this product commercially. His interest is said to have caused him to move to New Orleans, taking with him two steam engines, one of which was for grinding cottonseed. He did not, however, find conditions as he had hoped or expected and did not establish a mill as he apparently had intended. This same extract made reference to a Col. Clark, who about 1818 conducted some experiments on cottonseed oil for burning in lamps.[22]

The development of commercial crushing of cottonseed in the United States during the early years of the nineteenth century appears to have been somewhat retarded by the fact that most of the cottonseed produced had a tough hull covered by short lint fibers or fuzz; this made the seeds hard to grind, reduced the quantity of oil extracted (as the lint absorbed some of the oil), and lowered the quality of the cake. There was no machine for hulling cottonseed at that time and the development of such a machine is generally considered to have been an important step in the development of the commercial cottonseed crushing industry. The first patent for a cottonseed hulling machine was granted to J. Lineback of Salem, North Carolina, March 31, 1814, but since the records of this patent were destroyed by fire, with only an index reference remaining, little is known of the principles employed or whether the machine was ever used.[21] It was several years later that Francis Follet of Petersburg, Virginia, is said to have begun rather intensive efforts to develop a machine for hulling cottonseed. In January, 1829, a patent was obtained by Follet and in December of that year he obtained patents for an improvement in the machine. The extract from the *Niles Register* of 1829, referred to above, in discussing Follet's machine and how it operated, indicated that this machine would probably rank in importance second only to Whitney's gin.[22]

In 1829 Follet constructed and put in operation an oil mill at Petersburg; he and his partner, a man named Smith, are reported to have advertised the amount of seed their machines would hull and clean—also the yields of kernel, oil, and oil cake which could be expected from cottonseed.

[24] J. F. Moloney, *Proc. First Cotton Research Congress,* Waco, Texas, 1940, pp. 231–242.

They also claimed that because of cottonseed oil's cheapness and its usefulness it would supersede other oils for many purposes and that the oil cake was a highly nutritious feed for cattle.[25]

Their advertising apparently succeeded in demonstrating the practicability of extracting oil from cottonseed on a commercial basis, for it was reported that their patent rights for most of the southern states were sold to A. Plummer and Company and that this resulted in several more mills being constructed about 1833.[21] One of these mills was constructed at Natchez, Mississippi, one near Raleigh, North Carolina, another at Florence, Georgia, and one at Mobile, Alabama. The Natchez mill is said to have been one of the largest of these with a reported capacity (which, however, appears to be very doubtful) of from 1,000 to 2,000 gallons of oil per day. It is thought that this mill was operated for a few years and was then abandoned after heavy financial loss. Messrs. James Hamilton Cooper and Samuel Plummer of Georgia, along with Mr. Follet and a Major Anderson Miller of Louisville, Kentucky, were partners in this enterprise.[22]

Harry Hammond [26] stated that about 1832 a small oil mill was operating on an island off the Georgia coast. If such a mill existed it appears probable that the seed being crushed were those of the "naked" Sea Island cotton. These seed like those of Egyptian cotton were, for reasons previously indicated, easier to crush than the seed of Upland cotton. Apparently sizeable quantities of Egyptian cottonseed were being crushed in England and France at about this same time.

In 1835 papers of incorporation were granted by the Legislature of Louisiana to the "Cottonseed Oil Factory and Insurance Company" which was to be located in New Orleans. Little is known of what happened to this company. There is no record of it having constructed a mill.[25]

In the latter part of the 1840's Messrs. Frederick Good and William Wilbur of New Orleans made renewed efforts to establish a profitable cottonseed crushing enterprise. Their first efforts, at least, apparently failed, since Mr. Good is reported to have exhibited a small bottle of cottonseed oil which cost him $12,000.[22] About this same time Dr. Edward J. Coxe, also of New Orleans, attempted to convince producers and others of the large amount of waste which resulted from the failure to utilize the seed from the cotton crop of the United States, which at that time was around 1.3 million (478-pound) bales. Dr. Coxe was interested in increasing the market outlets for cottonseed products.[21]

In 1852 Mr. A. A. Maginnis of New Orleans, a manufacturer of linseed oil, crushed a small amount of cottonseed experimentally, the oil was intended for medicinal purposes and sold for $1 per gallon.[22] In this same

[25] *Encyclopedia Americana,* 1940 ed., Vol. 8, p. 85.
[26] H. Hammond, in "The Cotton Plant," *U.S. Dept. Agr. Expt. Sta. Bull.,* **33,** 336–370 (1896).

year Paul Aldigé, also of New Orleans, is said to have visited Marseilles, the seat of the French oil industry, for the purpose of studying the processes used there. In 1855 Messrs. Bradbury and Nautré of New Orleans are credited with having attempted to extract oil from cottonseed. In this same year Aldigé, P. J. Martin, F. M. Fisk, and Maginnis, all of New Orleans, constructed one or two mills in that city. About the same time the Union Oil Company constructed a large mill at Providence, Rhode Island. It was also at about this time that two mills were erected at Memphis, one at St. Louis, and a short time later another at Brooklyn, New York.[21, 22]

William Fee of Cincinnati invented and patented an improved huller in 1857 which played an important part in the rapid expansion of cottonseed crushing following the Civil War. His huller cut the seed open so that the divided kernels fell cleanly from the hull. Prior to this time, the hullers in operation subjected the seed to a grinding action which packed the hulls, fibers, and kernels together to such an extent that they could not be easily separated by screening. This huller is said to have used the same principles as those in use today, as did also a hydraulic press invented by Mr. Fee. Several marked advantages were claimed for this huller: (*a*) that it was capable of hulling 3 tons of seed per hour, which was a rate about 24 times faster than that of any other huller, (*b*) that by cutting instead of crushing or grinding the seed, some 30% more oil was derived from a given quantity of seed, and (*c*) that it would hull wet seed, including even seed completely drenched with water. This huller and the hydraulic press invented by Mr. Fee were in use in 1860 at mills in New Orleans, Memphis, St. Louis, Dayton, Cincinnati, and one or two places in Texas.[21]

Mr. Fee's patent is only one of about a dozen granted for hulling machines in the United States from 1855 to 1870. During this same period four patents were granted for the process of extracting oil from the seed, five for cleaning seed, and two for delinting the fiber. One of the delinting patents was granted to W. F. Pratt of Bridgewater, Massachusetts, June, 1869, and the other to G. W. Grader of Memphis, Tennessee, August, 1869.[21]

B. Legislation Relative to Seed Disposal

The marked expansion in cotton production and the increased volume of cotton handled by the individual cotton gin during the second quarter of the nineteenth century made the problem of disposing of the seed increasingly difficult. Where the seed were not hauled away, they often accumulated to such an extent that the gins would move away from the piles of seed which accumulated, just as portable saw mills move away from the refuse they create. Not only were the seed a nuisance in this respect, but the rotting seed often polluted streams and in some instances created the belief that they were the source of sickness among the inhabitants of the area. As a result, laws were passed in some states regulating the disposition

of the seed. In 1857, for example, the Mississippi Legislature passed a law requiring that any gin within a half mile of any city, town, or village should remove or destroy all cottonseed which resulted from the operation of the gin ". . . so that the same shall not prejudice the health of the inhabitants [22] of such city, town, or village." This law also prohibited the owner or proprietor of any cotton gin from throwing or permitting ". . . to be thrown the cottonseed from such gin into any river, creek, or other stream of water which may be used by the inhabitants for drinking or fishing."

The problem of disposing of the seed and the laws which were passed relating thereto probably gave considerable publicity to the large amount of agricultural produce which was going to waste and may have stimulated still greater interest in efforts to develop commercially profitable cottonseed crushing enterprises throughout the Cotton Belt. However, the mechanical difficulties in crushing cottonseed experienced in the years prior to the American Civil War were not the only obstacles which retarded the development of the industry. Perhaps one of the most important of these was the limited means of transportation. In many areas the cottonseed as well as other products had to move by horse-drawn vehicles over roads that were little more than trails. Also, the limited means of communication made the knowledge of any new developments in this field spread through the cotton-growing regions at a relatively slower rate.

C. Growth of the Industry following the Civil War

In view of the degree of development existing in mechanical processes and equipment, it is fairly evident that at the time of the outbreak of war between the states the stage was set for a rather rapid growth in the domestic cottonseed crushing industry. The census of 1860 reported a total of seven cottonseed crushing mills in operation in 1859, three of which were in Louisiana and one each in Missouri, Tennessee, New York, and Rhode Island. Not only did the Civil War temporarily retard the further expansion of the industry, but apparently four of the mills operating in 1859 went out of existence during the war.[21] From a long-time viewpoint, however, the war may have created a greater appreciation for the usefulness of cottonseed products, at least among the people of the South, than would have occurred had there been no such armed conflict. Reports indicate that the blockade of the South and the extreme scarcity of certain products stimulated the use of cottonseed oil for illumination, and cottonseed cake and cottonseed hulls for cattle feed. The indications are that it was during the Civil War that the usefulness of cottonseed hulls as a feed was discovered. Prior to that time and for a good many years thereafter, a large part of the hulls produced were used as fuel for operating the cottonseed mills.[24]

Soon after the Civil War, with the production of lint cotton and cottonseed again rapidly increasing, the erection of cottonseed oil mills also began to increase rapidly. Despite the disrupted state of conditions existing at the end of the war and particularly in the South, there were 26 mills in operation by 1869, 19 of which were in cotton-producing states (see Tables 3 and 4). These mills employed 664 persons and produced cottonseed products valued at slightly over $2,200,000—approximately $1,550,000 of which represented the value of cottonseed oil.[21] Ten years earlier the seven mills in operation at that time employed 183 persons and turned out products valued at $741,000.

Following 1869 the industry continued to expand quite rapidly until about the time of World War I when, in terms of number of mills, the peak was reached. In 1914 there were 882 cottonseed oil mills employing 21,810 workers, and the total value of the products was listed at $212,127,000. From that year to the present time there has been a rather steady decline in the number of cottonseed oil mills with the 1939 figure of 447

TABLE 3

Cottonseed Oil Mills: Number of Mills, Number of Wage Earners, Quantity of Seed Crushed, and Value of Products in the United States in Specified Years, 1859–1939[a]

Year	Establishments, number	Wage earners, number		Quantity of seed crushed		Value of products	
		Total	Average per mill	Total, 1000 tons	Average per mill, tons	Total, 1000 dollars	Average per mill, dollars
1859	7	183	26	—	—	741	105,857
1869	26	664	26	—	—	2,206	84,831
1879	45	3,319	74	235	5,222	7,691	170,909
1889	119	5,906	60	874	7,345	19,336	162,487
1899	369	11,007	30	2,479	6,718	58,727	159,151
1904	715	15,540	22	3,345	4,678	96,408	134,836
1909	817	17,071	21	3,269	4,001	147,868	180,989
1914	882	21,810	25	5,780	6,553	212,127	240,507
1919	711	26,766	38	4,013	5,644	581,245	817,503
1921	610	16,163	27	3,008	4,931	217,225	356,107
1923	511	12,745	25	3,308	6,473	226,388	443,029
1925	535	16,215	30	5,558	10,390	295,685	552,681
1927	547	18,434	34	4,654	8,508	276,338	505,189
1929	553	15,825	29	5,016	9,070	298,376	539,559
1931	504	12,268	24	5,328	10,571	181,347	359,816
1933	475	14,242	30	4,157	8,751	104,212	219,393
1935	458	13,226	29	3,818	8,336	187,887	410,234
1937	447	16,583	37	6,326	14,152	242,043	541,483
1939	447	15,191	34	4,151	9,286	171,476	383,616

[a] Compiled from reports of the Bureau of the Census as follows. 1859–1889: number of establishments, number of wage earners, and value of products from 1910 Census, *Manufactures*, Vol. VIII, p. 449, Table 273. 1899–1939: number of establishments, number of wage earners, and value of products from 16th Census of the U.S., 1940, *Manufactures*, Vol. II, Part 1, p. 758. Quantity of seed crushed is from *Cotton Production and Distribution.*

being only slightly over half as large as that of 1914. From 1859 to 1879 the average number of workers per mill increased almost three-fold and then in the next twenty years dropped back nearly to the 1859 average. Since 1904 the average number of workers per mill has varied between 21 and 38. Additional information on the number of mills, the number of workers, the quantity of seed crushed, the value of cottonseed products, and the distribution of the mills by states, for specified years may be found in Tables 3, 4, and 5.

TABLE 4

Number of Cottonseed Oil Mills in the United States, by States in Specified Years, 1859–1939[a]

State	1859	1869	1879	1889	1899	1909	1914	1919	1929	1939
Alabama	0	1	2	9	28	71	84	47	34	28
Arizona	0	0	0	0	0	0	1	3	6	6
Arkansas	0	1	4	8	20	44	43	35	31	26
California	0	0	0	0	0	0	1	4	8	8
Florida	0	0	0	2	1	5	4	3	1	1
Georgia	0	0	0	17	43	142	153	116	61	51
Illinois	0	0	0	0	1	2	2	3	4	4
Louisiana	3	6	12	7	24	43	37	28	23	21
Mississippi	0	4	8	13	41	87	67	49	50	41
Missouri	1	0	2	0	2	4	5	1	1	2
New Mexico	0	0	0	0	0	0	0	0	4	4
North Carolina	0	0	0	11	21	53	62	62	49	37
Oklahoma	0	0	0	0	12	39	60	51	45	29
South Carolina	0	1	0	17	50	103	97	81	38	30
Tennessee	1	4	9	15	17	20	24	22	20	15
Texas	0	2	4	13	103	194	233	200	176	144
Other states[b]	2	7	4	7	6	10	9	6	2	0
Total	7	26	45	119	369	817	882	711	553	447

[a] Compiled from reports of the Bureau of the Census.

[b] The number of mills for each of the "Other states" by years are: New York, 1859, 1; 1869, 2; 1889, 3; 1919, 1; Rhode Island, 1 in each of the years 1859–1929; Ohio, 1869, 4; 1879–1929, 1; Connecticut, 1879, 1; Virginia, 1879, 1; 1909, 1; 1914, 2; 1919, 1; Kentucky, 1889, 2; 1899, 3; 1909, 5; 1914, 2; 1919, 1; 1929, 2; Kansas, 1899, 1; 1909, 1; 1914, 1; New Jersey, 1909, 1; 1914, 2; 1919, 1.

Estimates, which are available on a comparable basis only from 1871–72 to date, indicate that with the expansion of the cottonseed crushing industry, the quantity of cottonseed crushed increased from 53,000 short tons in 1871, to 295,000 in 1881, and 1,068,000 in 1891. The increase continued, until in 1926 and in 1937, 6,300,000 tons were crushed—these two years being the years of record high domestic production of lint cotton and of cottonseed.

In 1871–72 the quantity of cottonseed crushed was equivalent to only about 4% of the total quantity of seed produced. Ten years later crushing had increased to about 13%, twenty years later to 27%, and thirty years later (1901) to 75%. By 1914 crushings as a percentage of production

TABLE 5

Value of Cottonseed Products in the United States, 1874–1943[a]

Year, beginning Aug. 1	Cottonseed products							
	Cottonseed oil		Cake and meal		Hulls		Linters	
	Total, 1000 dollars	Average per ton produced, dollars	Total, 1000 dollars	Average per ton produced, dollars	Total, 1000 dollars	Average per ton produced, dollars	Total, 1000 dollars	Average per ton produced, dollars
1874	1,590	132.50	940	31.33	—	—	—	—
1875	2,670	148.33	1,300	30.23	—	—	—	—
1876	1,770	118.00	840	24.70	—	—	—	—
1877	2,650	120.45	1,260	23.77	—	—	—	—
1878	2,400	88.90	1,410	22.03	—	—	—	—
1879	3,570	99.17	1,970	24.02	—	—	—	—
1880	2,770	98.92	1,840	28.75	—	—	—	—
1881	5,420	123.18	2,960	28.73	—	—	—	—
1882	7,060	119.66	3,580	26.13	—	—	—	—
1883	6,020	100.33	3,830	27.75	—	—	—	—
1884	6,980	93.07	3,490	20.06	—	—	—	—
1885	6,710	77.13	4,260	21.09	—	—	—	—
1886	8,050	77.40	4,770	19.63	—	—	—	—
1887	11,520	92.90	5,610	19.48	—	—	—	—
1888	13,980	117.48	6,390	22.99	—	—	—	—
1889	10,130	77.33	6,270	20.49	—	—	—	—
1890	11,460	74.42	8,330	23.27	—	—	—	—
1891	11,540	72.13	8,980	24.01	—	—	—	—
1892	10,080	63.80	8,550	23.23	—	—	—	—
1893	16,600	77.57	11,900	23.75	—	—	—	—
1894	13,420	53.25	11,450	19.51	—	—	—	—
1895	11,480	53.40	8,700	17.33	—	—	—	—
1896	11,720	48.03	14,540	25.51	—	—	—	—
1897	12,610	40.03	14,070	19.14	—	—	—	—
1898	13,180	37.34	14,780	17.96	—	—	—	—
1899	21,390	61.11	16,030	18.13	3,190	2.73	1,800	85.71
1900	26,080	72.04	16,270	19.25	3,990	3.50	1,890	67.50
1901	33,210	74.63	21,930	19.49	6,320	4.25	1,520	44.70
1902	40,560	87.79	23,310	20.01	5,390	3.50	2,030	48.33
1903	39,000	85.34	24,840	21.49	5,710	3.74	4,380	95.22
1904	31,340	62.43	27,770	20.42	5,590	4.61	4,610	86.81
1905	26,400	55.93	29,250	23.00	5,110	4.50	4,190	83.80
1906	43,050	74.74	39,140	25.04	8,840	6.35	3,350	45.89
1907	33,390	86.50	23,300	22.34	6,370	6.87	2,920	49.49
1908[b]	44,090	80.16	33,580	22.51	6,080	4.57	2,340	30.00
1909	55,230	112.48	35,910	27.08	9,810	7.61	4,770	64.46
1910	80,340	127.52	44,660	24.92	11,370	8.27	6,250	65.79
1911	66,580	88.07	49,720	23.11	9,890	6.02	5,150	38.72
1912	69,100	99.28	45,970	23.00	9,710	6.31	7,450	51.38
1913	81,020	111.75	59,810	26.94	11,210	8.01	7,630	49.87
1914	80,540	93.65	57,740	21.81	8,450	5.04	6,150	30.00
1915	87,940	140.48	53,860	28.01	12,340	10.11	26,120	117.66
1916	153,419	217.92	74,586	33.52	13,994	14.44	45,193	142.12
1917	217,902	332.17	97,352	47.08	18,878	18.95	26,604	98.53
1918	227,316	343.38	116,119	53.51	17,917	15.76	22,228	100.13
1919	209,668	345.99	119,039	65.51	11,095	9.71	12,336	84.49
1920	84,650	129.43	58,298	32.64	10,059	8.01	3,560	33.58
1921	71,508	153.78	49,898	36.84	8,949	9.55	6,619	69.67
1922	84,818	168.96	59,037	39.70	12,200	12.93	17,199	118.61
1923	88,093	179.78	59,300	39.07	12,737	13.55	22,007	137.54

(Table continued)

TABLE 5 (*concluded*)

Year, beginning Aug. 1	Cottonseed products							
	Cottonseed oil		Cake and meal		Hulls		Linters	
	Total, 1000 dollars	Average per ton produced, dollars	Total, 1000 dollars	Average per ton produced, dollars	Total, 1000 dollars	Average per ton produced, dollars	Total, 1000 dollars	Average per ton produced, dollars
1924	126,665	180.43	79,173	37.25	13,749	10.33	21,268	98.92
1925	138,652	171.60	81,508	31.39	12,649	8.17	23,218	86.96
1926	142,242	150.68	72,476	25.52	8,882	4.79	16,684	60.01
1927	132,372	179.30	80,582	38.49	9,995	7.57	24,878	101.96
1928	133,906	166.96	90,706	39.76	12,842	9.39	27,793	90.24
1929	114,892	146.14	82,296	36.87	12,103	8.75	20,149	67.16
1930	91,638	127.10	58,623	27.08	10,474	8.04	8,969	37.68
1931	57,546	67.94	33,071	13.77	5,237	3.47	6,694	26.04
1932	47,234	65.34	29,467	14.08	4,681	3.57	5,931	26.96
1933	48,409	74.32	39,513	20.92	7,513	6.81	16,490	69.58
1934	91,849	165.70	54,023	33.46	10,260	11.24	21,606	89.65
1935	101,454	174.36	38,753	22.29	6,568	6.65	20,970	80.04
1936	123,189	180.64	65,783	32.38	10,472	9.15	29,739	87.47
1937	121,510	123.90	62,843	22.20	8,917	5.48	18,927	43.02
1938	86,601	122.88	47,194	23.32	7,123	6.13	12,267	36.95
1939	77,561	117.16	54,003	28.69	8,728	8.27	18,920	58.94
1940	77,482	108.83	52,586	26.92	8,771	7.92	27,397	75.47
1941	151,730	242.77	67,558	38.55	7,909	7.98	33,521	93.37
1942	177,837	254.05	73,005	36.60	9,460	8.72	37,586	91.23
1943	157,545	254.93	88,802	48.41	11,863	12.80	31,704	89.81

[a] Total value of cottonseed oil, cake and meal, hulls, and linters are from *Cotton Production and Distribution*, Bureau of the Census Bulletin 166, season of 1928–29, pp. 72–73, and subsequent issues.

[b] The figures of the 13th Census are not shown on this table because they do not represent a single-growth year.

reached a new record high of 81, and since then crushings have ranged between 68 and 90% of production. On the average, during the period since the beginning of World War I, the mills have crushed about 80% of the crop, the remainder of the seed being used for planting, feed, and fertilizer.

Estimates of the quantity of cottonseed oil produced in the United States, also available only since 1871, show that there has been comparatively little increase in the quantity of oil obtained per ton of seed crushed during the past period of seven and one-half decades. Consequently, the production of cottonseed oil has changed about in proportion to the quantity of cottonseed crushed. In the case of cake and meal, however, the indicated production per ton of seed crushed averaged close to 700 pounds for the period from 1871 to 1903, and then increased materially. From the latter date to 1909 the average was 812 to 814 pounds, and from 1910 through 1944 the average ranged between 872 and 993 pounds with no particular evidence in the latter period of any upward or downward trend (see Table 6).

TABLE 6

Production of Cottonseed, Cottonseed Oil, Cake and Meal, Hulls, Linters, and Cottonseed Crushed in the United States, 1871–1944[a]

Year, beginning Aug. 1	Cottonseed			Cottonseed products							
				Cottonseed oil		Cake and meal		Hulls		Linters	
	Production, 1000 short tons	Crushings, 1000 short tons	Proportion of total production crushed, %	Total, 1000 short tons	Average per ton of seed crushed, lb.	Total, 1000 short tons	Average per ton of seed crushed, lb.	Total, 1000 short tons	Average per ton of seed crushed, lb.	Total, 1000 short tons	Average per ton of seed crushed, lb.
1871	1223	53	4.3	8	302	18	680	—	—	—	—
1872	1621	52	3.2	8	308	18	692	—	—	—	—
1873	1718	74	4.3	11	298	26	752	—	—	—	—
1874	1567	84	5.4	12	286	30	714	—	—	—	—
1875	1909	123	6.4	18	292	43	700	—	—	—	—
1876	1826	98	5.4	15	306	34	694	—	—	—	—
1877	1994	150	7.5	22	294	53	706	—	—	—	—
1878	2106	181	8.6	27	298	64	708	—	—	—	—
1879	2425	235	9.7	36	306	82	688	—	—	—	—
1880	2822	182	6.4	28	308	64	704	—	—	—	—
1881	2280	295	12.9	44	298	103	698	—	—	—	—
1882	3033	392	12.9	59	300	137	700	—	—	—	—
1883	2450	396	16.2	60	302	138	696	—	—	—	—
1884	2427	499	20.6	75	300	174	698	—	—	—	—
1885	2828	578	20.4	87	301	202	698	—	—	—	—
1886	2802	694	24.8	104	300	243	700	—	—	—	—
1887	3056	823	26.9	124	301	288	700	—	—	—	—
1888	3074	794	25.8	119	300	278	700	—	—	—	—
1889	3318	874	26.3	131	300	306	700	—	—	—	—
1890	3802	1023	26.9	154	300	358	700	—	—	—	—
1891	3967	1068	26.9	160	300	374	700	—	—	—	—
1892	2956	1050	35.5	158	300	368	700	—	—	—	—
1893	3297	1431	43.4	214	300	501	700	—	—	—	—
1894	4448	1677	37.7	252	300	587	700	—	—	—	—
1895	3174	1435	45.2	215	300	502	700	—	—	—	—
1896	3778	1628	43.1	244	300	570	700	—	—	—	—
1897	4878	2101	43.1	315	300	735	700	—	—	—	—
1898	5120	2353	46.0	353	300	823	700	—	—	—	—
1899	4152	2479	59.7	350	282	884	714	1169	943	21	19
1900	4500	2415	53.7	362	300	845	700	1139	944	28	24
1901	4226	3154	74.6	445	282	1125	714	1487	942	34	22
1902	4729	3269	69.1	462	282	1165	712	1541	942	42	25
1903	4379	3241	74.0	457	282	1156	714	1528	942	46	28
1904	5967	3345	56.1	502	300	1360	812	1213	726	53	32
1905	4700	3131	66.6	472	302	1272	812	1135	726	50	32
1906	5898	3844	65.2	576	300	1563	814	1393	724	73	38
1907	4931	2565	52.0	386	300	1043	814	927	762	59	46
1908	5883	3670	62.4	550	300	1492	814	1330	724	78	42
1909	4442	3269	73.6	491	300	1326	812	1289	788	74	44
1910	5156	4106	79.6	630	306	1792	872	1375	670	95	46
1911	6970	4921	70.6	756	308	2151	874	1642	668	133	54
1912	6087	4580	75.2	696	304	1999	872	1540	672	145	64
1913	6286	4848	77.1	725	300	2220	916	1400	578	153	64
1914	7155	5780	80.8	860	298	2648	916	1677	580	205	70
1915	4963	4202	84.7	626	298	1923	916	1220	580	222	106
1916	5085	4479	88.1	704	314	2225	993	969	433	318	149

(Table continued)

TABLE 6 (*concluded*)

Year, beginning Aug. 1	Cottonseed			Cottonseed products							
				Cottonseed oil		Cake and meal		Hulls		Linters	
	Production, 1000 short tons	Crushings, 1000 short tons	Proportion of total production crushed, %	Total, 1000 short tons	Average per ton of seed crushed, lb.	Total, 1000 short tons	Average per ton of seed crushed, lb.	Total, 1000 short tons	Average per ton of seed crushed, lb.	Total, 1000 short tons	Average per ton of seed crushed, lb.
1917	5012	4252	84.8	656	309	2068	972	996	467	270	133
1918	5341	4479	83.9	662	296	2170	969	1137	508	222	104
1919	5069	4013	79.2	606	302	1817	906	1143	570	146	76
1920	5966	4069	68.2	654	322	1786	878	1256	619	106	54
1921	3528	3008	85.3	465	309	1355	901	937	623	95	67
1922	4330	3242	74.9	502	309	1487	918	944	582	145	94
1923	4503	3308	73.5	490	296	1518	918	941	569	160	101
1924	6050	4605	76.1	702	305	2126	923	1331	578	215	97
1925	7150	5558	77.7	808	291	2597	934	1547	557	267	100
1926	7989	6306	78.9	944	299	2840	901	1854	588	278	92
1927	5758	4654	80.8	738	317	2093	900	1320	567	244	109
1928	6319	5061	80.1	802	317	2282	902	1368	541	308	127
1929	6406	4016	78.3	786	313	2232	890	1384	552	300	124
1930	6028	4715	78.2	721	306	2165	918	1304	553	238	105
1931	7310	5328	72.9	847	318	2401	907	1511	567	257	100
1932	5815	4621	79.5	723	313	2093	906	1312	568	220	99
1933	5511	4157	75.4	652	313	1889	909	1103	531	237	118
1934	4256	3550	83.4	554	312	1614	910	913	514	241	141
1935	4634	3818	82.4	582	305	1739	911	988	518	262	143
1936	5472	4498	82.2	682	303	2031	903	1144	509	340	156
1937	7844	6326	80.6	980	310	2830	895	1626	514	440	144
1938	4950	4471	90.3	704	315	2023	905	1161	519	332	154
1939	4869	4151	85.3	662	319	1882	907	1055	508	321	160
1940	5286	4398	83.2	712	324	1954	888	1107	504	363	171
1941	4553	4008	88.0	625	312	1753	874	992	495	359	186
1942	5202	4498	86.5	700	311	1995	887	1085	482	412	190
1943	4688	3955	84.4	618	313	1834	928	927	469	353	185
1944	4902	4253	86.8	662	312	1954	918	984	462	375	176

[a] Cottonseed production 1871 through 1927 from *Cotton Acreage, Yield, and Production, 1866–1938*, Agricultural Marketing Service, Crop Reporting Board, Sept., 1940; data for 1928–1944 from *Farm Production, Farm Disposition, and Value of Cotton and Cottonseed and Related Data, 1928–1944*, Bureau of Agricultural Economics, Oct., 1945. Quantity of cottonseed crushed, production of cottonseed oil, cake and meal, and hulls from *Cotton Production and Distribution*, Bureau of the Census Bulletins 90, season of 1907, and 166, season of 1928–29, p. 72–73, and subsequent issues. Production of linters in net weight bales for 1912 to date are from *Cotton Production and Distribution*, Bulletin 135, p. 16, and subsequent issues. Production for earlier years interpolated from production in running bales as reported in Bulletin 166, p. 72–73. Average production of oil, cake and meal, hulls, and linters for 1916 to date are from *Cotton Production and Distribution*, Bulletin 137, and subsequent issues. Data for earlier years are calculated.

The quantity of hulls and of linters produced in the United States have been estimated only from 1899 to date. Except for the war periods, the production of linters per ton of seed crushed showed a rather steady upward trend from 1899 to date. In 1899 production of linters averaged 19 pounds per ton. In 1913 it averaged 64 pounds; in 1923, 101 pounds; in

1938, 154 pounds. During both the World Wars I and II the strong demand for linters resulted in a production per ton of seed crushed which was materially in excess of that in the years immediately prior to these wars. The average in 1916 was 149 pounds; and the average in 1942 was 190 pounds.

The production of hulls per ton of seed crushed has declined greatly since 1899. In that and each of the next four years the official estimates show the average output of hulls per ton of seed crushed as a little over 940 pounds, whereas during the 1930's the average annual production per ton of seed was between 508 and 568 pounds. During World War II the annual average dropped to a low of 462 pounds per ton of seed crushed. Since about 1910 the downward trend in the output of hulls per ton of seed is to a considerable extent accounted for by the upward trend in the quantity of linters produced per ton of seed crushed.

IV. Development of Markets for Cottonseed Products

The rapid expansion in the cottonseed crushing industry of the United States immediately after the Civil War was based on the use of machines and techniques largely developed prior to the war. The practicability of profitably producing cottonseed products apparently had already been adequately demonstrated. It must have been quite generally believed that at least those mills which were skillfully operated and advantageously located would be able to produce cottonseed products at a profit even with little or no further fundamental technological improvements. This would appear to be borne out by the fact that the number of mills in the United States increased from only 3 at the end of the war to 26 in 1869. It was, by this time, clearly evident that the industry had passed out of its experimental stages.

From about this time on the problem of developing increased market outlets became highly important. There was a large supply of cottonseed to draw on—the 1869 production of cottonseed totaled about 1.1 million tons—and the knowledge and machinery was available for crushing the seed and producing oil and other products on a basis which was comparatively efficient for that stage of the nation's industrial development. The only thing needed at this point to bring about large additional increases in the quantity of seed crushed was an increase in market outlets which would absorb the additional quantities of cottonseed products without occasioning too great a decline in their prices. In view of the improvements continually being made in the industry's machinery and techniques and in transportation facilities, considerable expansion in the industry was by no means contingent upon increased markets sufficient to maintain the existing prices for cottonseed products. In fact, from 1874–75, the first year for which comparable data are available, until near

TABLE 7

Estimated Uses of Cottonseed Oil in the United States, 1874–75 to 1911–12[a]

Year, beginning Sept. 1	Uses, million pounds							
	Soap making	Salad oil	Cooking and baking	Lard compound	Oleomargarine	Packing sardines	Other purposes	Total
1874	10.0	4.0	—	—	—	—	1.4	15.4
1875	15.9	6.0	—	—	—	—	3.0	24.9
1876	1.2	6.0	—	—	—	—	2.9	10.1
1877	4.0	6.0	—	—	—	—	1.8	11.8
1878	4.0	3.2	—	—	—	—	0.9	8.1
1879	4.0	3.2	—	—	—	—	1.2	8.4
1880	7.9	4.0	—	4.0	2.0	—	1.0	18.9
1881	31.8	6.0	—	19.9	2.0	—	1.8	61.5
1882	47.8	7.9	2.0	39.8	4.0	—	1.8	103.3
1883	23.9	11.9	2.0	29.9	4.0	—	0.8	72.5
1884	19.9	8.0	2.0	29.8	6.0	2.0	2.7	70.4
1885	47.8	9.9	3.2	39.8	6.0	2.0	2.5	111.2
1886	63.7	9.9	3.2	59.7	8.0	3.2	2.4	150.0
1887	71.6	11.9	4.0	79.6	8.0	3.2	3.1	181.4
1888	79.6	11.9	4.0	79.6	9.9	4.0	6.0	195.0
1889	35.8	11.9	4.0	59.7	9.9	4.0	3.0	123.3
1890	51.7	11.9	4.8	99.5	11.9	2.0	6.6	188.4
1891	59.7	11.9	4.8	99.5	11.9	4.0	6.2	198.0
1892	35.8	13.9	4.8	99.5	13.9	4.0	6.0	177.9
1893	67.7	13.9	6.0	119.4	13.9	4.0	6.3	231.2
1894	71.6	15.9	6.0	199.0	15.9	6.0	7.8	322.2
1895	39.8	17.9	6.0	119.4	15.9	6.0	7.4	212.4
1896	43.8	19.9	7.9	171.1	19.9	6.0	9.0	277.6
1897	39.8	21.9	11.9	167.2	27.9	11.9	18.4	299.0
1898	39.8	29.8	13.9	179.1	19.9	6.0	9.6	298.1
1899	47.8	31.8	15.9	238.8	10.0	6.0	8.9	359.2
1900	55.7	39.8	17.9	286.5	8.0	6.0	5.8	419.7
1901	131.3	51.7	33.8	477.6	8.0	6.0	14.1	722.5
1902	119.4	61.7	45.8	457.7	8.0	9.9	16.0	718.5
1903	129.4	95.5	59.7	437.8	6.0	13.9	68.5	810.8
1904	179.1	111.4	67.7	398.0	4.0	13.9	63.8	837.9
1905	119.4	107.5	79.6	437.8	4.0	11.9	37.4	797.6
1906	99.5	87.6	99.5	358.2	4.0	9.9	23.9	682.6
1907	79.6	59.7	79.6	238.8	2.0	2.0	9.9	477.6
1908	87.5	59.7	79.6	338.3	6.0	6.0	22.9	600.0
1909	159.2	79.6	159.2	398.0	15.9	8.0	67.9	887.8
1910	179.1	99.5	159.2	437.8	19.9	11.9	21.8	929.2
1911	179.1	79.6	179.1	445.8	27.9	11.9	13.3	936.7

[a] G. M. Weber and C. L. Alsberg, *The American Vegetable Shortening Industry*, Stanford Univ. Press, Stanford, Univ., Calif., 1934, p. 317. The data in this publication were taken from reports of Aspegren & Co., *Cotton Oil*, 3rd ed., New York, 1909, and 6th ed., New York, 1913—the data being converted from barrels of 398 pounds to the barrel.

the end of the century there was a downward trend in the average annual value per ton of cottonseed oil and cottonseed cake and meal. While other chapters of this book will consider in detail the uses of cottonseed products in recent years, it seems appropriate at this point to review rather briefly some of the more important aspects in the early development of markets for cottonseed products.

TABLE 8

Cottonseed Oil Exported from United States and Estimated Uses Made of Such Exports, 1874–75 to 1911–12[a]

Year, beginning Sept. 1	Uses, 1000 barrels (398 pounds)							
	Salad oil	Cooking and baking	Soap making	Lard compound	Artificial butter	Packing sardines and other fish	Other purposes	Total
1874	4.0	—	2.0	—	—	—	1.85	7.85
1875	2.5	—	1.5	—	—	0.20	1.11	5.3
1876	20.0	—	10.0	—	—	0.50	1.60	32.1
1877	50.0	—	35.0	—	0.5	0.75	7.55	93.8
1878	53.0	—	40.0	—	0.5	0.75	6.75	101.0
1879	60.0	0.5	60.0	—	1.0	1.0	9.1	131.6
1880	30.0	0.5	25.0	—	1.0	0.5	7.6	64.6
1881	6.0	0.3	5.7	—	0.8	0.2	0.4	13.4
1882	3.0	—	3.0	—	0.5	0.3	1.0	7.8
1883	35.0	0.5	25.0	0.5	1.0	0.5	5.3	67.8
1884	60.0	1.0	50.0	0.5	1.0	0.5	7.0	120.0
1885	60.0	1.0	48.0	0.5	1.0	0.5	6.6	117.6
1886	40.0	0.5	30.0	0.5	1.0	0.5	4.0	76.5
1887	44.0	0.5	34.0	0.5	1.0	0.5	4.2	84.7
1888	24.0	0.5	20.0	0.5	1.0	0.5	4.0	50.5
1889	150.0	2.0	80.0	2.0	5.0	1.5	10.5	251.0
1890	100.0	3.0	70.0	4.0	10.0	2.0	18.0	207.0
1891	120.0	4.0	100.0	6.0	15.0	3.0	13.0	261.0
1892	100.0	4.0	30.0	8.0	15.0	3.0	18.0	178.0
1893	100.0	5.0	120.0	10.0	20.0	4.0	22.0	281.0
1894	150.0	6.0	160.0	15.0	35.0	6.0	28.0	400.0
1895	130.0	7.0	140.0	20.0	40.0	7.0	22.0	366.0
1896	170.0	8.0	200.0	25.0	70.0	10.0	29.0	512.0
1897	200.0	9.0	220.0	30.0	150.0	15.0	32.0	756.0[b]
1898	300.0	10.0	400.0	50.0	150.0	20.0	32.0	962.0
1899	230.0	11.0	320.0	50.0	180.0	20.0	33.0	874.0[b]
1900	300.0	12.0	280.0	75.0	200.0	25.0	38.0	930.0
1901	160.0	13.0	50.0	60.0	100.0	20.0	20.0	432.0
1902	250.0	14.0	130.0	80.0	150.0	20.0	26.0	670.0
1903	220.0	15.0	90.0	80.0	150.0	30.0	25.0	600.0[b]
1904	360.0	16.0	200.0	100.0	250.0	30.0	44.0	1000.0
1905	230.0	20.0	150.0	100.0	260.0	30.0	50.0	840.0
1906	220.0	25.0	140.0	100.0	235.0	20.0	60.0	800.0
1907	210.0	30.0	130.0	100.0	225.0	20.0	59.0	774.0
1908	350.0	35.0	170.0	140.0	250.0	30.0	19.0	994.0
1909	120.0	40.0	50.0	80.0	130.0	20.0	10.0	450.0
1910	180.0	45.0	100.0	90.0	120.0	20.0	9.0	564.0
1911	200.0	60.0	250.0	200.0	180.0	35.0	25.0	950.0

[a] G. M. Weber and C. L. Alsberg, *The American Vegetable Shortening Industry*, Stanford Univ. Press, Stanford Univ., Calif., 1934, p. 318. Compiled from reports of Aspegren & Co., *Cotton Oil*, 3rd ed., New York 1909, and 6th ed., New York, 1913.

[b] Correct totals of items shown are 656,000 for 1897, 844,000 for 1899, and 610,000 for 1903. The errors may be in totals or in one or more components.

A. Cottonseed Oil

1. History of Cottonseed Oil Utilization

At the time that cottonseed oil extraction was still in the experimental stage it was thought that the oil, which has always been by far the most

important cottonseed product, would be used quite extensively both as an illuminant and as a lubricant. That cottonseed oil would become important in both uses is said to have been freely predicted once a successful method of extraction was developed.[24] However, the development of the petroleum industry, which was just getting under way in the late 1850's, prevented either illuminant or lubricant from ever becoming important applications of cottonseed oil.

In France, where the utilization of cottonseed developed somewhat earlier than in the United States, cottonseed oil was refined and used for edible purposes somewhat prior to 1850.[27] It was apparently a little after this before it was so used in the United States. One of the early edible uses for this oil was in admixture with lard, apparently for the primary purpose of tempering lard for consumption in extreme climates. About this time cottonseed oil is said to have also been tested as a salad oil and found to compare very favorably with the best olive oils.[21] These tests apparently stimulated the demand for the oil for mixing with lard and with olive oil. Nevertheless, from this period until about the middle of the 1870's most of the cottonseed oil produced apparently went into soap. According to estimates of Aspegren and Company as published in *The American Vegetable Shortening Industry*[28] about two-thirds of the cottonseed oil used in the United States in 1874–75 was for soap making and most of the remainder for salad oil (see Tables 7 and 8). Aspegren's estimates of the uses of the cottonseed oil exported during the same year indicate a substantially smaller proportion being used for soap making and a much larger proportion for use as salad oil. When both the domestic utilization and the exports are combined, these estimates indicate that slightly more than half the oil was used for soap making and about 30% for salad oil. Exports in 1874–75 represented only about 17% of the domestic production of cottonseed oil.

Due at least in part to the fact that cottonseed oil in the early years of its commercial production had been used largely for inedible purposes, there was apparently considerable prejudice against it when it was first used for mixing with lard or as a salad oil. For some years its use for these purposes was kept a secret, or at least efforts were made to avoid any publicity regarding its use.

It is said that the early exports of American cottonseed oil for use as a human food were sent largely to Mediterranean ports for mixing with olive oil. In 1875–76 Italy alone accounted for approximately half of the total exports from the United States. Between this date and 1879–80, annual exports to Italy increased from about 1 million pounds to slightly

[27] *Encyclopedia Britannica,* 14th ed., Vol. 6, 1939, p. 584.

[28] G. M. Weber and C. L. Alsberg, *The American Vegetable Shortening Industry,* Stanford Univ. Press, Stanford Univ., Calif., 1934, pp. 317–318.

over 23 million pounds, but despite the marked increase she accounted for a somewhat smaller percentage of the total exports than in the early year. This rapid increase in cottonseed oil imports into Italy caused Italian olive growers to demand protection from their government. The cottonseed oil was not only being mixed with olive oil, but in some instances 100% cottonseed oil is said to have been sold as olive oil. It apparently was also sold under its own name, particularly among low income classes, as a competitor of more expensive olive oil. Widespread adulteration is said to have been practiced not only in the products consumed in Italy and other Mediterranean countries, but also in the products exported from this area. It is quite commonly recognized that a considerable proportion of the so-called olive oil imported into the United States at that time represented cottonseed oil which had previously been exported from this country.[29]

In 1881 the Italian import duty on cottonseed oil was increased from 6.5 to 16.6 cents per gallon, and shortly thereafter exports from the United States to Italy began declining sharply. In 1882–83 official figures show no exports to Italy. The total for the year of only 3 million pounds exported was 94% smaller than in 1879–80. A part of the decline in total exports also resulted from reduced shipments to other European countries, apparently due at least in part to several years of low corn prices in Europe, which perhaps resulted in expanded hog production.[29]

The marked drop in cottonseed oil exports in the early 1880's caused the domestic price of cottonseed oil to drop in relation to the price of lard from an average of about 0.8 cent per pound (based on New York wholesale prices of lard and of prime summer yellow cottonseed oil) above lard in 1878 and 1879, to more than 5.1 and 4.7 cents, respectively, below lard in 1881 and 1882. This stimulated the domestic use of cottonseed oil in a number of products, especially soap and lard compounds. According to the Aspegren estimates, 4 million pounds of cottonseed oil were used domestically in lard compounds in 1880–81, almost 20 million pounds in 1881–82, and nearly 40 million pounds in 1882–83. In these same years cottonseed oil used domestically in soap was estimated at about 8, 32, and 48 million pounds, respectively. These two uses combined represented 85% of the total domestic use in 1882–83 compared with only 63% of the total in 1880–81.[28]

In 1882–83 lard compound, according to the Aspegren estimates, was utilizing nearly two-fifths of the total cottonseed oil consumed in the United States, as compared with negligible quantities three years earlier. It was in about 1880 that cottonseed oil began to be used in significant

[29] G. M. Weber and C. L. Alsberg, *The American Vegetable Shortening Industry*, Stanford Univ. Press, Stanford Univ., Calif., 1934, pp. 15–16.

quantities in the production of margarine, a product introduced into this country from France during the 1870's.[24]

The rapid increase in the use of cottonseed oil in the so-called "adulteration" of lard and the increase in the use of this oil in the production of margarine, a butter substitute, created considerable concern among the hog producers and dairymen, both of which sought legislation against it. Moloney,[24] economist of the National Cottonseed Products Association, has pointed out: "At the time, there was probably just cause for complaint. Mixtures of cottonseed oil and lard were sold under the name of 'refined lard'." He indicates that, while this practice was widely discussed in the trade journals, consumers generally were probably unaware that they were not buying 100% lard. About this same time also it is said that margarine was often sold to consumers as butter. This situation together with the fact that ". . . the period was one of widespread adulteration of food and other commodities . . ." resulted in a natural demand for reform, both from those who wanted to protect the consumer and from those interested in the market outlets for individual commodities.

Moloney reports that the politically strong dairy groups had considerable success in their campaign against margarine: "In several states the production and sale of the product were prohibited and, in 1886, a Federal law was passed. This statute imposed annual license taxes of $600 on manufacturers, $480 on wholesalers, $48 on retailers, and a product tax of 2 cents a pound. Provisions were also made for packaging and labeling. While there existed ample reason for the regulatory features of the law, an examination of the Congressional hearings and debate reveals that the suppression of competition was a strong motive behind the tax provisions. A similar bill affecting mixtures of lard with other fats and oils passed the House in 1890 but the Senate [24] never took action on it." However, even before the latter bill was passed by the House some of the larger "lard refiners" announced that their products would be labeled "lard compounds."

The discriminatory federal and state legislation no doubt seriously retarded the United States' production of margarine and the use of cottonseed oil for this purpose. Nevertheless, according to Aspegren's estimates the quantity of cottonseed oil used in this country for making margarine continued to increase until 1897–98. The estimates also indicate a continued and marked upward trend in the quantity going into lard compound.

During the 1880's and the first part of the 1890's the greatest percentage increase in the domestic market outlets for cottonseed oil was in lard compound, salad oil, and margarine. Its use in soap making, which after 1883 was second in importance to its use in lard compound, showed a downward trend from 1888–89 to about the end of the nineteenth century. In 1882–83 the Aspegren figures show that there were about 2 million pounds of cotton-

seed oil being used for cooking and baking other than that going into lard compounds. The quantity of cottonseed oil so used showed comparatively little increase over the next fifteen years, but in the last half of the 1890's began increasing quite rapidly. By 1911–12, the last year for which the Aspegren estimates are available, 179 million pounds of cottonseed oil were estimated to have been used for "cooking and baking" in addition to 446 million pounds used in lard compound, these two uses together representing two-thirds of the cottonseed oil used in the United States. In that same year soap making accounted for 19%, salad oil 9%, margarine 3%, sardine packing 1%, and other uses 1%. Moloney reported that just before the beginning of World War II about 65% of the total domestic consumption of cottonseed oil was for shortening, 8% for margarine, and 18% for miscellaneous food products, including salad dressings, mayonnaise, salad oil, and food packing oil. The balance, mostly off-grade oil and foots, was used for inedible products.[24]

2. Development of Oil Processing Methods

Cottonseed oil, unlike some other vegetable oils, is very nearly inedible in the crude form. Like many other oils, it is much more suitable for edible purposes after it has been subjected to the processes of bleaching and deodorization, and for some purposes it is improved by hydrogenation. Thus the development and perfection of these processes has been very important in extending markets for the oil although few of those writing of the development of the industry have given any attention to them. Some of the early history of these processes is, therefore, given briefly here. An additional treatment of them will be found in Chapters XVII and XVIII.

It was apparently toward the end of the eighteenth century that considerable experimentation first began in an effort to develop processes which would eliminate the objectionable features of certain oils. Weber and Alsberg [30] report that two methods of oil refining were worked out about the turn of the century, one employing strong sulfuric acid and the other, strong caustic alkali. They also indicate that between 1840 and 1846 European patents were issued on at least four additional methods, one of which (an alkali method) was probably used to some extent prior to 1800.

Caustic alkali, which subsequently became widely used, evidently did not come into general use for oil refining much before 1850. The date of its introduction in the United States is not generally known although it is believed to have been used in cottonseed oil refining fairly soon after

[30] This and the following paragraphs relating to the technology of refining, bleaching, and deodorizing fats and oils are largely based on pages 251 to 259 of G. M. Weber and C. L. Alsberg, *The American Vegetable Shortening Industry,* Stanford Univ. Press, Stanford Univ., Calif., 1934, which contain an excellent review of the history of these and other processes.

the domestic industry began its rapid growth. It was not until 1883 or later, however, that the N. K. Fairbank Company began using caustic soda instead of the more expensive caustic potash. David Wesson, then a young chemist just employed by this company, is credited with having brought about this shift.

The first method used for bleaching oil was by simply exposing it to sunlight, this being the method that seems to have been generally employed in the early days of the domestic industry. Other early methods of bleaching oil included the blowing of air and steam through the oil, a combination of exposure to the sun and heating by means of steam coils, running the oil over warm metal plates, and bleaching by the action of chemicals. The chemical methods in use around the middle of the nineteenth century were unfit for food oils. Some cottonseed oil is said to have been bleached by this method for sale to miners for use in lamps.

Fuller's earth seems to have been proposed for bleaching wax during the eighteenth century and to have been used for treating vegetable oils early in the nineteenth century. In 1880 a United States patent was granted to Alexander W. Winter for the purifying of certain vegetable oils and animal fats, using pulverized fuller's earth. About this same time Allbright and Eckstein of the N. K. Fairbank Company are said to have begun using fuller's earth for bleaching cottonseed oil and lard, and in 1886 a patent covering the use of this material was issued to Allbright. Allbright's patent was different from the one issued to Winter. It covered the use of fuller's earth in combination with steam, which greatly reduced the loss of oil retained in the earth. This method is said to have soon superseded all others.

Even though bleaching eliminated the objectionable color of cottonseed oil for certain uses, the oil still needed deodorizing in order to overcome its objectionable flavor and odor. Deodorization was successfully carried out in about 1891 by Eckstein by blowing high-pressure steam through the oil. This method was subsequently improved by James Boyce, chemist of the American Cotton Oil Company. About 1900 Wesson, after leaving the American Cotton Oil Company, made further improvements in the deodorizing process by treating the oil with steam while maintaining it under a vacuum. This gave the oil better keeping qualities as well as an improved odor and flavor.

The hydrogenation process had a very important effect on the cottonseed oil industry, inasmuch as it provided a means for preparing a plastic shortening from liquid oils without the necessity of employing beef fat or other naturally hard fat as a stiffening agent. Hence, it made shortening manufacture independent of meat packing, and, in effect, fostered an entirely new industry based on cottonseed products alone.

Although the modern hydrogenation process had its origin in the clas-

sical research of Sabatier and Senderens, in the period 1897–1905, it was not applicable to fatty oils until the development of liquid-phase hydrogenation by Normann.[30a] The Normann patent, issued in 1903, passed to the British firm of Joseph Crossfield & Sons, from which Procter & Gamble Company acquired American rights in 1909. The new all-hydrogenated cottonseed oil shortening, "Crisco," was placed on the market by the latter firm in 1911. Subsequent litigation invalidated the basic patents under which this product was manufactured, and the way was opened for general use of the hydrogenation process, which was soon adopted by all American manufacturers.

B. Cottonseed Cake Meal

Estimates of the United States' production of cottonseed cake and meal extend back to 1871. Estimates relating to cottonseed hulls and linters begin in 1899. Since the latter date cottonseed cake and meal has continued to rank second to cottonseed oil in value, exceeding the combined value of hulls and linters by a substantial margin.

Among the early references to the domestic uses of cottonseed cake and meal is a letter[30b] published in the December, 1829, issue of the *Southern Agricultural Registrar of Rural Affairs,* which mentions oil cake as ". . . an article which is known to every farmer as a nutritious food for cattle." While this is undoubtedly a great exaggeration, it would seem to indicate that cottonseed oil cake, as it was referred to in the early years of the industry, was used at least to some extent at that time for cattle feed.

It was many years later that Tompkins[31] indicated a considerably different situation prevailing with regard to the use of cottonseed cake and meal. Writing in 1901 he stated that at first the domestic demand for cottonseed meal was entirely as a fertilizer and that it was so used both for direct application to the soil and as one of the ingredients for making commercial fertilizers. He further stated that in the 1880's about 90% of the meal produced in the southeastern states was used for fertilizer, about 5% was fed to cattle, and the remainder was exported. But in the Southwest (where little fertilizer was used) he reported that about 25% of the cake and meal produced at that time went for cattle feeding in this country and approximately 75% was exported to Europe, also for cattle feed. In this connection it is significant that for the year ending June 30, 1894, total exports of cottonseed cake and meal have been officially reported at 245,000 short tons, equivalent to approximately half of the

[30a] W. Normann, Brit. Pat. 1,515 (1903).

[30b] A. L. Ward, *Proc. First Cotton Research Congress,* Waco, Texas, 1940, pp. 249–258.

[31] D. A. Tompkins, *Cotton and Cotton Oil,* published by the author, Charlotte, N. C., 1901, pp. 240–241.

total production of cottonseed cake and meal in 1893–94. Tompkins indicated that at the time he was writing (1901) cattle feeding had become an intensive business and that in the Southeast and Southwest combined about 35% of the cottonseed meal produced was fed to cattle, about an equal amount was used for fertilizers, and the remainder was exported for feed. The official export figures, however, reveal that in 1901–02 exports of cottonseed cake and meal were running just a little under 50% of the total domestic production.

A survey made by the Census Office of the Department of the Interior in 1880 showed that cottonseed cake and meal were apparently being used quite extensively for feed at that time.[32] Of the 20 cottonseed oil mills from which replies to the mail questionnaire were received (about half of the total mills in operation), nearly all indicated that cake and meal was being used for this purpose. Two of the Texas mills reported that most of it was being used for feed. Kilgore[33] pointed out in 1896 that (according to a U.S. Department of Agriculture report of 1864) cottonseed meal was fed in the United States, at least to some extent, earlier than 1860, and in England (*Journal of the Royal Agricultural Society of England,* 1864, Part 1, page 235) prior to 1864.

According to Curtis[34] cottonseed cake feeding trials were conducted with sheep as early as 1877 at Woburn, England, and with bullocks from 1878 to 1890, and a number of other foreign experiments were conducted with dairy cattle about this same time. He stated that in this country a number of agricultural experiment stations conducted experiments in the feeding of cottonseed products to livestock during the latter part of the nineteenth century, but apparently little, if anything, was done prior to 1880. The North Carolina Station, which was organized in 1876, first mentioned cottonseed meal in its annual report of 1881.[30]

One of the first bulletins published in the United States relating to cottonseed meal as a livestock feed was Bulletin No. 3 (July, 1889) of the Tennessee Agricultural Experiment Station, which was established in 1882. This bulletin[35] also referred to cottonseed hulls—it concluded that the ration for feeding cattle should contain from 25 to 35 pounds of hulls and from 5 to 8 pounds of cottonseed meal. Some of the comments appearing in this bulletin on ". . . the practical as well as scientific features connected with the use of cottonseed hulls and meal as a stock food" are worth recording: "At least as early as 1870, we have good evidence of local and individual cases of feeding the cottonseed hulls to livestock, but

[32] 10th Census of the U.S., 1880, *Cotton,* Part 1, pp. 43–51.

[33] B. W. Kilgore, "The Cotton Plant," *U.S. Dept. Agr. Expt. Sta. Bull.,* **33,** 385–387 (1896).

[34] R. S. Curtis, *Cottonseed Meal—Origin, History, and Research,* Raleigh, N. C., 1938, pp. 89–90.

[35] W. E. Stone, *Tennessee Agr. Expt. Sta. Bull.,* **3,** 41–48 (1889).

probably the first attempts at systematically feeding a ration of hulls and meal on a large scale have been made within four or five years. These cases have been local and confined to the vicinities of the oil manufacturing centers like Memphis, New Orleans, Houston, Little Rock, Raleigh, Atlanta, and hence have not attracted general attention." The author then reported that inquiries had been made of the number of head of cattle maintained in this way during the preceding (1888–89) winter, at specified places. The number given both for Atlanta and Memphis was 5,000. A. J. Vick and Company was reported to have fed 10,000 head at the different mills of the Southern Cotton Oil Company during this season.

Exports of cottonseed cake and meal reached an all-time high in 1908–09, when they totaled 875,000 tons and were equivalent to almost three-fifths of the total production. Since then exports of cottonseed cake and meal have shown a rather pronounced downward trend and in most years since the beginning of the Agricultural Adjustment program in 1933–34 imports of cottonseed cake and meal have exceeded exports.

For most years since World War I data are available giving reasonably good indications of the quantity of cottonseed meal used for fertilizer on cotton farms. For a few years estimates were also made (by the National Fertilizer Association) of the total quantity used as fertilizer. The indications are that during this period the quantities so used have been relatively small. In 1931-32, the year in which cottonseed meal used for fertilizer apparently reached a peak, 458,000 tons are estimated to have been used for fertilizer on cotton farms and 465,000 tons on all farms. The total used for fertilizer, including that used by fertilizer manufacturers, was 507,000 tons. The latter, however, represented only about 23% of the total domestic disappearance of cottonseed cake and meal for that year. Since then there has been a rather sharp downward trend; in 1944–45, 34,000 tons were used for this purpose, which is equivalent to only 5% of the total domestic disappearance.

While almost all of the cottonseed cake and meal used in the United States has been used for feed or fertilizer, only small quantities have been used for human food. McMath [36] reports that this use was first suggested in 1876 when J. W. Allison placed a cottonseed flour on the market, which was especially recommended for use in those diets requiring a low starch content. This flour has apparently never been produced in anything but small quantities. McMath wrote in 1940: "Though at the present time, the production of cottonseed flour is small, its uses limited, and the yield per ton of seed low, it promises in time, after further research has improved its qualities and given it new uses, to take its place as one of the valuable by-products of cottonseed."

[36] C. W. McMath, *Proc. First Cotton Research Congress,* Waco, Texas, 1940, pp. 243–248.

C. Cottonseed Hulls

Tompkins [31] and others state that the first use made of cottonseed hulls was as a fuel to run the oil mills. He claims that the ordinary mill with a seed capacity of 40 tons or more made enough hulls to supply the total fuel requirements of the mill and that a mill of this size with an economical power plant produced a surplus of hulls. Thus in the early years of the industry the mills producing more than they needed for running the mill were confronted with the problem of disposing of the surplus. Since they were very bulky and light in relation to their fuel value, transportation of the hulls to other plants located at a distance from the oil mill was uneconomical. According to Tompkins a ton of hulls, which was equal in fuel value to only a quarter of a ton of coal, occupied (in the loose state) about 30 times as much space as a ton of coal. He also indicated that the use of cottonseed hulls was on a rather limited scale prior to about 1885 to 1890.

According to the survey made by the Census Office in 1880 (page 38), cottonseed hulls were more generally used for stock feed in 1880 than was suggested by Tompkins. Of the 20 cottonseed mills reporting, more than half indicated that hulls were being used in their locality for feed. Nineteen of the 20 reported that the hulls were also being used for fuel, and several reported at least some hulls being used for packing. This survey also indicated that at some mills the ashes of the hulls were being sold or otherwise disposed of for use as a fertilizer. Attention is again directed to the Tennessee Station Bulletin previously referred to on page 38, which stated that cottonseed hulls were in local and individual cases being fed to livestock as early as 1870. It should be recalled also that the first attempts at systematically feeding rations of hulls and meal on a large scale were made only within four or five years from the time this bulletin was published in 1889.

Since about the end of the nineteenth century it is believed that a relatively small proportion of the cottonseed hulls produced in this country have been used for fuel and a large proportion for feed. Data are not generally available on the relative importance of the different uses of cottonseed hulls. It is generally recognized, however, that at times sizeable quantities are used as stuffing or packing of one kind or another. In addition there are a wide variety of uses in which small quantities of this material are utilized (see Chapter XXIII).

D. Linters

Prior to the invention of the linter machine in the late 1860's (it was patented in 1869) and its general adoption throughout the industry, there was little or no production of linters. While production estimates are

available only since 1899, important quantities were produced and consumed as early as 1880. In the survey made by the Census Office in 1880 referred to on page 38, practically all the mills from which linters were received were using some kind of linter machine. In replying to the question "Do you find it a paying process, whether as to the value of the shoddy produced or the increased yield of oil?" one mill reported that the value of the "lint" so obtained was the most profitable part of the business. Several other mills indicated at least by implication that this material was being sold.

It seems probable that in the very early days of the commercial production of linters it was largely used for stuffing materials, wadding, batting and the like, and for low-grade yarns. It may also have been mixed with wool shoddy or with virgin wool and with other materials. Hammond,[26] in 1896, in writing of the handling and uses of cotton and cottonseed, stated that linters were ". . . used to make paper, hats, carpet yarns, cheap cloth, and for most of the purposes to which ordinary lint cotton is applied, but of course commands a lower price." In a bulletin [37] published by the United States Bureau of the Census in 1906 appears the statement that from linters ". . . are manufactured cotton batting, carpets, cheap yarns, rope, twine, and it is also used for upholstering purposes."

By 1898, the first year for which export statistics are available, the United States was exporting substantial quantities of linters. For that calendar year 30,000 bales of 500 pounds each were shipped abroad, and by 1904 exports had increased to 60,000 bales. From July, 1905, until the middle of 1914, linters were included in the official reports as a part of the exports of lint cotton. Estimates of total domestic consumption, which first became available in 1909, indicate that in that year exports were probably more than 100,000 running bales—production being estimated at more than 300,000 running bales and domestic consumption at only 177,000 bales. In 1914–15 exports totaling more than 200,000 bales were shipped abroad. This was equivalent to a little over half the quantity reported as having been consumed in the United States.

During World War I considerable quantities of linters were employed in the production of explosives; linters at that time were the principal source from which nitrocellulose was obtained for smokeless powder. *American Industry in the War,* a report of the War Industry Board,[38] reported that despite the establishment of a "Cotton Linter Pool" by means of which the maximum cotton linters capacity of the country was turned directly to war use, there still ". . . would not have been enough cellulose material for the powder programs of ourselves and the Allies." Consequently,

[37] "Cotton Production," *Bureau of the Census, Bull.,* **40,** 71 (1906).

[38] B. Baruch, *American Industry in the War,* a report of the War Industries Board, Govt. Printing Office, Washington, D. C., 1921, p. 173.

machinery was installed in one of the largest privately-owned plants and in two of the government plants for use of the combination of cotton linters and hull fiber or wood pulp. Also, one of the government plants used old cotton rags successfully. According to this report: "These combined plans would have made possible the full smokeless powder program laid down for 1919."

As will be seen in Chapter XXIV, the rayon industry has in recent years provided a market outlet for substantial quantities of cotton linters. This industry was first established on a commercial basis in the United States about 1910 or 1911 and from that time on has grown very rapidly. It is not known to what extent linters were used in the early period of the development of the domestic rayon industry, but the indications are that linters have never constituted a very important proportion of the raw material used by this industry—wood pulp having been the main source of cellulose.

V. Trade Associations and Their Relation to the Industry's Development [39]

A. Original Association

Those familiar with the history of the domestic cottonseed crushing industry no doubt will agree that during the last half century various trade associations within the industry—state, interstate, and national—have played a very prominent part in the industry's development. According to Moloney [39] the first such association was formally organized under a constitution and by-laws adopted at a meeting in Cincinnati in 1878. Although there are few records of this original association now available, the late Louis N. Geldert, for many years editor of the *Cotton Oil Press*, left a brief account of its history. For five successive years following its organization, conventions were held in Memphis, New Orleans, Cincinnati, New York, and Chicago.

There were 103 cottonseed crushing mill representatives in attendance at the 1882 meeting in New York. The business session, which was held in the Board Room of the Equitable Life Insurance Society at 120 Broadway, was presided over by President Jules Aldige of New Orleans. The convention banquet that year was held at the world-famous Delmonico's and was tendered to the delegates by members of the New York oils trade.

[39] The author is indebted to the National Cottonseed Products Association and the Texas Cotton Seed Crushers' Association for material for this section supplied from their files. He is particularly indebted to John F. Moloney, Economist of the National Cottonseed Products Association, and to Miss Bennette Wallin, Secretary-Treasurer, Texas Cotton Seed Crushers' Association. Mr. Moloney was good enough to supply an advance copy of his article "A Half Century of Progress—The Story of the National Cottonseed Products Association," prepared for the May 4, 1946, issue of the *Cotton and Cotton Oil Press*, from which was taken a considerable amount of material for that part of this section dealing with the Interstate and National Associations.

The original "Cotton Seed Crushers' Association" appears to have gone out of existence following the Chicago meeting in 1883. Moloney reports that following this meeting, ". . . nothing more is heard of an industry-wide organization until Louis K. Bell conceived the idea of an association founded on 'broader lines than the old Association'." Mr. Bell is said to have conceived the idea for such an association while returning to New York from the Annual Convention of the Oil Mill Superintendents of Texas, this organization being the predecessor of the National Oil Mill Superintendents' Association. After discussing this idea with his associates, Mr. Bell, at that time editor of the *Oil, Paint and Drug Reporter,* published an editorial in this magazine on May 17, 1897, urging that the industry organize an industry-wide association.

B. Texas Association [40]

Bell has frequently been called the "father of the Association," meaning the Interstate Cotton Seed Crushers' Association, which later became the National Cottonseed Products Association. This distinction can be attributed to the part he played in stimulating representatives of the industry into action rather than to originality in conceiving the benefits of such an organization to the industry. The Association which was organized in Cincinnati had previously existed for at least five years, from 1878 to 1883, and at the time of Bell's editorial the Texas Cotton Seed Crushers' Association had been an active organization for about three years. Probably Mr. Bell had some knowledge of both these Associations. Some of those participating in the organization and operation of the Texas Association from the time of the preliminary meeting at the Windsor Hotel, Dallas, April 7, 1894, were active in the formulation and early development of the Interstate Cotton Seed Crushers' Association.

Reports of the proceedings of subsequent annual sessions of the Texas Cotton Seed Crushers' Association show that the Dallas Morning News for April 8, 1894, carried a report of the preliminary meeting held the preceding day. According to this account the meeting was attended by some 37 representatives of mills (as well as others) and was presided over by Dr. Benjamin Dabney of Bonham, Texas; the secretary of the meeting was E. H. Young of McKinney, Texas. After the adjournment of the meeting Secretary Young [41] stated: "The objective of the meeting was for the purpose of establishing a cotton oil exchange as a medium of information for all the mills regarding the market value of products, as well as for the interchange of general experience relating to the improvement of

[40] The Texas Association is only one of a number of active state associations, but is the oldest. This and its close relation to the development of the Interstate and National Associations accounts for the attention given it.

[41] *Proc. 25th Annual Session of the Texas Cotton Seed Crushers' Association,* Galveston, Texas, 1919.

the business." Nine directors were chosen to devise a plan of organization and report to a meeting to be held in Waco on May 10, 1894.

The organization of the Association was effected, the constitution and by-laws adopted, and officers elected at the May 10 meeting which was held at the Pacific Hotel in Waco. The officers for 1894–95 were: President, Dr. Benjamin Dabney, Bonham; Vice-President, H. L. Scales, Corsicana; Secretary, Robert K. Erwin, Itasca; and Treasurer, S. C. Collier, Dallas.[41]

According to Section 3 of the original constitution and by-laws, the objectives of the Association were ". . . to promote social intercourse, to foster the industry, to diffuse accurate and useful information among its members, to reform abuses in conduct of business, and to protect its members against unjust and unlawful exactions." Originally membership in the organization was open to ". . . any manufacturer engaged in making cottonseed oil" with each oil mill limited to one member.

The original rules of the Texas Cotton Seed Crushers' Association were adopted at a special meeting at Galveston, August 12, 1895. A copy of these now on file at the Association's headquarters in Dallas shows that there were 36 rules governing the classification, packaging, measurement, delivery, and shipment of cottonseed products. One of these rules was two sentences in length and the other 35 were each composed of only one sentence.

Since 1894–95 there have been numerous changes in the constitution and by-laws and in the trading rules of the Texas Association. In 1936 the Association was incorporated and since then it has operated under a new constitution and by-laws adopted at that time. Since 1929 the trading rules of this Association have been administered by the National Cottonseed Products Association, the Texas Association having no separate set of rules since that time.

The early activities of the Texas Association are indicated by the active committees for the annual term beginning June, 1901. At that time there were six committees as follows: Executive, Rules, Arbitration, Freight Rates on Fuel Oil, Legislation, and Grievances. The first three of these were standing committees and the last three, special committees.

By the time the Association had held its twenty-fifth annual session in 1919 its rules had expanded in number to 45, several of which had from 8 to 15 sections. At that time the Association had a total membership of 347, including 194 mills, 12 refineries independent of crude mills, 92 regular members, and 49 associate members. The secretary of the Association reported in that year the addition of 45 new members with 23 members having withdrawn, giving a net increase in the membership for the year of 22 members.

A letter from Miss Bennette Wallin, Secretary-Treasurer of the Texas

Association,[42] contains a few comments on some of the activities of the Association and its relation to the development of the cottonseed crushing industry. She points out that over a period of more than a half century the ". . . Texas Cotton Seed Crushers' Association has participated in practically every phase of agricultural and livestock development in the State of Texas. . . . For instance, when faced with the loss of export markets for cottonseed products it was the Texas Association that established the educational service; which, later, became national in scope and which, now, is maintained by the National Cottonseed Products Association. This service was begun in Texas, July 1, 1926."

Miss Wallin said also that since 1921–22: ". . . the Texas Association has maintained a Traffic Department, . . . which has had a great deal to do with the industry's development," and that "cooperation with Texas Agricultural Colleges has been one of our chief activities over a period of years. In 1924, our Association began a cooperative program with the Department of Chemistry and Chemical Engineering at the A & M College of Texas, by supplying men from the cottonseed crushing industry to give a series of lectures to students in cotton oil milling. In 1926, we began to equip a Cotton Oil Mill Laboratory . . . at the A & M College . . . and, beginning in 1929, the College—with our Association cooperating—began sponsoring an annual short course for oil mill operators. . . . Under an appropriation from the Texas Cotton Research Committee (established by our State Legislature in 1941) a new Cottonseed Products Research Building was erected in 1944, on the A & M College campus. Our Association is displacing, as rapidly as possible, the equipment in the old laboratory with new standard oil milling equipment secured 'on loan' from various machinery companies."

This Association also sponsors Graduate Fellowships at the A & M College of Texas and at Texas Technological College, and in January, 1945, added an Agricultural Director to its staff, who works in close cooperation with the various ". . . agricultural organizations in an intensive, concerted program to save and improve the soil and secure increased per-acre yields of all crops."

C. Interstate and National Associations

The publication of the editorial in the *Oil, Paint and Drug Reporter* in 1897 suggesting an industry-wide association was apparently just what was needed to spur others who also had been thinking about such an organization into action. Mr. F. W. Brode, a broker of Memphis, and some friends are said to have been discussing the subject at the time the editorial appeared. A short time later a committee was selected to make arrangements for a meeting to be held in Nashville, Tennessee (which city was

[42] *Private communication,* April 5, 1946.

holding its Centennial Exposition) as had been suggested by Mr. Bell. This committee was composed of E. M. Durham of Vicksburg, Mississippi, Chairman; L. W. Haskell of Savannah, Georgia; and R. K. Erwin of Waxahatchie, Texas. The meeting was held on July 16 and this date was designated as "Cottonseed Oil Day" by officials of the Centennial Exposition. Those attending the meeting (which included 45 members of the industry) elected E. M. Durham and C. Fitzsimmons as temporary chairman and secretary, respectively. An organization committee composed of L. W. Haskell, R. K. Erwin, J. H. DuBose, George B. Alexander, and J. M. Baker recommended the establishment of the permanent organization to be known as the Interstate Cotton Seed Crushers' Association. The organization committee submitted a proposed set of rules and by-laws and the objectives of the organization. Following the delegates' acceptance of the committee's recommendations, E. M. Durham was elected President for the ensuing year. M. Frank of Atlanta, Georgia, was elected Vice-President, and Robert Gibson, Secretary-Treasurer.

On July 21 and 22, 1898, the Interstate Cotton Seed Crushers' Association met in Atlanta, Georgia, and adopted a constitution, a set of by-laws, and 29 rules for the government of transactions in cottonseed products. Article I of this original constitution specified that the object of the Association ". . . shall be to protect and to promote the interests of the cotton-seed industry, especially to enlarge the markets for the sale of products, to the end that both the planter and manufacturer may be benefited." The remainder of the constitution, together with the by-laws, the rules for the government of transactions, and a list of members as of August 15, 1898, are all contained in the souvenir pamphlet distributed at the Forty-fourth Annual Convention of the National Cottonseed Products Association in 1940. Copies of this pamphlet are readily available and have been widely distributed.

The original constitution of the Interstate Cotton Seed Crushers' Association provided that: "Every cottonseed oil mill should be entitled to one representative. Each president or executive officer of two or more mills shall be entitled to become a member in addition to the representative of each of his individual mills." It is reported that there were 35 original subscribers to the constitution and by-laws. From this small membership the Association grew quite rapidly and in 1914 when the number of crushing mills reached an all-time peak, the number of regular members totaled 225, exclusive of 55 associate members, the associate members representing those who were privileged to attend all the meetings but were not permitted to vote.[43] As of May 1, 1946, on the eve of the fiftieth anniversary of the original Interstate Association, the number of regular and associate

[43] *Proc. 19th Annual Meeting Interstate Cotton Seed Crushers' Association,* San Antonio, Texas, 1913, p. 44.

members in its successor, the National Cottonseed Products Association, totaled 525 and 65, respectively.

Many of the activities of the Interstate and National Associations have been quite similar to those of the Texas Association. This was particularly true in the early years of these organizations. In this connection it is significant to note that Robert Gibson, who was Secretary of the Texas Association from August, 1895, until his death in 1927, was secretary-treasurer of the Interstate Association from its beginning until 1924, when at the age of 90, he tendered his resignation as secretary. He retained his position as treasurer in the latter association until his death.

In reporting on the activities of the Interstate Association, Moloney [39] points out that in addition to the development of trading rules the Association established a Bureau of Publicity in 1905, one year after the establishment of such a bureau by the Texas Association. Despite rather limited financial support, the Publicity Bureau prepared several pamphlets and circulars and ". . . initiated a voluminous series of correspondence with government officials, publications, and experiment stations." From this beginning the Publicity Bureau continued to operate until 1927 when the Educational Service of the Texas Association was taken over and expanded. Since then, the activities previously handled by the Publicity Bureau have been carried on by the Educational Service.

In a recent article about the Educational Service—which is now generally considered as one of the most important activities of the National Cottonseed Products Association—Franke [44] points out that the function of the Educational Service is admittedly to ". . . sell cottonseed products . . ." but that the ". . . program is built on the broad educational base that encompasses every farming and ranching pursuit that either directly or indirectly benefits agriculture." The Service works in close cooperation with various federal and state agricultural agencies, ". . . privately-owned demonstration farms, breeders, county agents, vocational teachers, 4-H and FFA clubs, agricultural fairs and livestock expositions, livestock associations, etc."

In addition to activities relating to trading rules, publicity, and education service, the Interstate Association and its successor the National Association have maintained a legislative committee ever since 1905 when this committee was first recommended. As the name implies, this committee was interested in legislation affecting the welfare of the industry. It also took an active interest in such matters as import duties and other trade barriers imposed by foreign countries which affected the export market for cottonseed products.

One of the many other activities with which the Association has concerned itself is the publication or sponsorship of a monthly bulletin or

[44] P. Franke, *Acco Press,* **24,** No. 1, 3–4 (Jan., 1946).

magazine. In 1917 the Executive Committee of the Association approved the appointment of Louis N. Geldert as Assistant to the President and as editor of the Association's new monthly bulletin which was later named the *Cotton Oil Press*. This magazine was published by the Association until 1926 when it was sold outright to Mr. Geldert, who continued to edit and publish it until his death in September, 1935. Shortly after this the magazine was sold to the *Cotton and Cotton Oil News*, of Dallas. The name of the combined magazines was changed to the *Cotton and Cotton Oil Press*. This publication, like the *Cotton Oil Press* before it, has been designated by the National Association as its official publication.

Over the years there have been many special committees appointed by the Association to deal with problems of various kinds affecting the welfare of this important industry. In 1924 a committee on cottonseed grading was established. In this same year a committee was appointed to cooperate with the U.S. Department of Agriculture in developing grade standards for linters. Two years later standard grades for cotton linters were established by the U.S. Department of Agriculture, and in 1931 official government standards for cottonseed were established.

At the 1925 convention of the Association there was a substantial reorganization of the Association, including the establishment of the position of general manager, who, under the supervision of the executive committee, would have complete responsibility for the Association's activities. Christie Benet was appointed to this position and following this the activities of the Association were expanded still further.

In 1928 the convention of the Interstate Cotton Seed Crushers' Association authorized the appointment of a committee to negotiate with the Texas Association with the view of combining the trading rules and port facilities of the two associations. This committee, in collaboration with a similar committee appointed by the Texas Association, worked out a plan which was presented to the 1929 convention and adopted subject to approval by the Texas Association. On July 8, 1929, the convention reassembled in New Orleans, approved the reorganization plan, and adopted the name, National Cottonseed Products Association. Benet continued as chief administrative officer, with A. L. Ward as educational director, and George Bennett as secretary-treasurer. The activities of the National Cottonseed Products Association continued about the same as the activities of the Interstate Association.

Shortly after the National Association was organized the Senate passed a resolution (in October, 1929) calling for an investigation of the cottonseed industry by the Federal Trade Commission. From June, 1930, to February, 1932, a number of separate hearings were held. In May, 1933, the Commission reported to Congress that there was a suspicion of the legality of certain of the activities and practices in the cottonseed industry,

that it had rescinded its approval and acceptance of the Trade Practice Conference Rules for the cottonseed industry, and ordered complaints to be issued in accordance with provisions of the Federal Trade Commission Act.[45] According to Moloney, [39] the Commission issued formal complaints against the Association in 1934 but never took any action on them, and finally dismissed the complaints on December 21, 1939.

During the depression of the early 1930's the activities of the National Association were considerably restricted, one of the principal retrenchments being the discontinuance of the Educational Service by the National Association. Shortly after this action was taken, however, the Texas Association elected Ward as executive vice-president and authorized him to continue at least some of the educational work. The Oklahoma Association also agreed to continue to provide financial support for this work. In 1935 the National Association again assumed full responsibility for the Educational Service and from that time up to the present the general program of the Association has continued to expand.

[45] *Report on Cottonseed Industry,* letter from the Chairman of the Federal Trade Commission, Govt. Printing Office, Washington, D. C., 1933, Senate Document No. 209, Part 13, p. XV.

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CHAPTER II

PRODUCTION AND CONSUMPTION OF COTTONSEED AND COTTONSEED PRODUCTS

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I. World Production and Consumption

A. COTTONSEED PRODUCTION

Among the many cotton-producing nations of the world, six countries, the United States, India, the Soviet Union, Brazil, China, and Egypt account for more than nine-tenths of the total commercial cottonseed output; and when the production of Uganda, Turkey, the Anglo-Egyptian Sudan, Peru, Mexico, Argentina, and Chosen is taken into consideration, virtually all available supplies of cottonseed are covered. Although cotton is of importance within the domestic economies of some of these minor producers, such as Uganda and the Anglo-Egyptian Sudan, the quantity of seed processed by each of them is insignificant when compared with the output of any of the six principal nations.

The outbreak of World War II checked abruptly a prewar expansion in world cotton acreage and the quantity of seed ginned. In the face of domestic market maladjustments and the loss of foreign outlets for lint cotton, output in all the principal producing countries declined markedly over the course of the war. Reflecting this decrease, estimates place 1945–46 cottonseed output at less than 11 million tons, lower than at any time in the preceding fifteen years. The situation within the United States, where a traditional 30–40% of the world's total cottonseed supply originates, emphasizes the extent of this curtailment. The 1945–46 U.S. cottonseed crop totaled only 3.7 million tons, the lowest since 1921.

However, indications are that, with the possible exception of the United States, the decline resulted almost entirely from wartime conditions, and when normal trade channels reopen, an increasing cottonseed output may again be expected. Prewar increments warrant this expectation. Both Brazil and the U.S.S.R. doubled their cottonseed output during

TABLE 9

World Production of Cottonseed in Recent Years[a]

Country	Cottonseed production, thousand short tons												
	1933–34	1934–35	1935–36	1936–37	1937–38	1938–39	1939–40	1940–41	1941–42	1942–43	1943–44	1944–45	1945–46
United States	5,511	4,256	4,634	5,472	7,844	4,950	4,869	5,286	4,553	5,202	4,688	4,902	3,703
India	2,027	1,923	2,346	2,493	2,288	2,019	1,963	2,432	2,451	1,821	2,103	1,417	1,800[b]
China	1,499	1,720	1,248	2,224	1,633	1,224	981	1,246	551	[c]	[c]	800[b]	800[b]
U.S.S.R.	959	849	1,246	1,827	1,907	2,017	2,094	1,896	1,609	[c]	[c]	[c]	[c]
Egypt	864	761	849	915	981	748	781	822	747	377	326	426	490
Brazil	389	732	765	904	1,043	1,123	1,102	1,205	1,294	970	1,277	1,280	724[b]
Peru	142	160	156	148	156	149	153	133	120	133	96	160[b]	160[b]
Uganda	133	118	150	158	187	154	138	165	105	50[b]	80[b]	110[b]	[c]
Argentina	118	181	220	135	141	127	125	103	171	174	231	187	[c]
Mexico	116	105	139	178	149	130	131	121	151	188	209	215	184
Iran	80	64	82	73	88	110	99	83	72	46	26	24	30[b]
Anglo-Egyptian Sudan	73	127	91	122	133	131	105	106	131	100	90[b]	150[b]	[c]
Turkey	71	97	134	131	155	189	172	126	128	165	165[b]	150[b]	110[b]
Chosen	69	66	91	101	102	89	86	108	[c]	[c]	[c]	[c]	[c]
Total	12,051	11,159	12,151	14,881	16,807	13,160	12,799	13,832	12,083[d]	9,226[d]	9,291[d]	9,821[d]	8,001[d]

[a] Official statistics, except for noted estimates. [b] Estimate. [c] No data available. [d] Incomplete.

the period 1933–34 to 1940–41, with their combined production supplying 26% of the world total in the latter year, contrasted with 13% in 1933–34. A less notable expansion occurred in nearly all other cotton raising areas, but as the area under cotton cultivation, at least among the other major producers, had reached a practical maximum by 1933–34, these minor increases in output resulted either from a more efficient level of operations or from much smaller additions in acreage than those which occurred in Brazil and the U.S.S.R.

B. Cottonseed Processing

Wide-scale commercial crushing of cottonseed is carried on by only a limited number of countries. Among these nations the United States is by far the most important processor of cottonseed, and is the only country maintaining adequate statistics covering all cottonseed products for any considerable period. The United States is also the world's most important consumer of these products, and in addition to utilizing by far the bulk of the domestic output, uses minor amounts imported from foreign sources.

In other cotton-producing countries, consumption of fats and oils in general is considerably lower than in the United States, and cottonseed oil is not considered as vital a commodity as in this country. For example, China's normal seed supplies appear sufficient to provide better than 450 million pounds of oil annually, yet, little or no information regarding processing is available. In all likelihood oil production there is principally in the hands of the cotton farmers operating the most primitive type of extraction equipment.

Both Brazil and the U.S.S.R. do utilize large quantities of seed in commercial oil manufacture, but in the case of the U.S.S.R. no data relative to this output have been furnished since 1934 when a reported 198 million pounds of oil was processed. Brazilian oil production has increased markedly in recent years, reaching a peak of 247 million pounds in 1941. This rise resulted from a combination of factors. While domestic cottonseed supplies were expanding markedly, olive oil imports were becoming increasingly scarce, and local consumption of all vegetable oils was on the increase. Egyptian production of cottonseed oil also increased rapidly during the past several years, and again shortages of imported oils was of prime importance in bringing about this development. The output of cottonseed oil in Egypt, which reached a record 203 million pounds in 1942, was utilized exclusively to meet domestic needs during the war period, although prior to that time fairly substantial quantities of oil were exported.

Among the major cotton-producing nations India appears to be the only country where the bulk of the cottonseed produced is neither crushed

TABLE 10

Cottonseed Oil Output by Major Producing Countries in Recent Years[a]

Country	Cottonseed oil output, thousand pounds								
	1937	1938	1939	1940	1941	1942	1943	1944	1945
United States	1,626,215	1,677,673	1,389,792	1,274,192	1,391,574	1,385,867	1,312,531	1,132,462	1,276,253
China[b]	589,310	439,270	341,310	273,420	343,790	146,630	[c]	[c]	[c]
United Kingdom[d]	233,387	215,451	181,027	86,699	38,886	27,912	4,940	3,483	[c]
Brazil	145,654	149,377	166,899	207,715	248,831	168,374	178,121	228,791	72,000
Egypt	[c]	[c]	[c]	110,230	121,253	202,625	142,503	153,000	163,600
Mexico	42,134	35,391	36,755	32,483	41,178	56,261	62,831	64,610	55,225
Peru	[c]	[c]	37,478	35,494	40,013	38,832	45,062	33,829	38,902
Japan[d]	35,555	21,259	3,277	[c]	[c]	[c]	[c]	[c]	[c]
Argentina	27,071	27,867	34,356	36,402	22,549	40,471	50,000[e]	70,000[e]	55,000[e]
Chile[d]	14,905	17,300	13,641	12,509	2,496	1,896	12	[c]	[c]
Iran	[c]	[c]	[c]	[c]	[c]	1,411	529	992	900[e]
U.S.S.R.[f]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
Total	2,714,231[g]	2,583,588[g]	2,204,535[g]	2,069,144[g]	2,250,570[g]	2,070,279[g]	1,796,529[g]	1,687,167[g]	1,661,880[g]

[a] Official statistics, except for noted estimates.
[b] Oil equivalent seed production minus exports.
[c] No data available.
[d] Oil equivalent seed imports.
[e] Estimated.
[f] Information on cottonseed oil in the U.S.S.R. available for following years only: 1927–28, 142 million pounds; 1930, 145 million pounds; 1931, 168 million pounds; 1932, 194 million pounds; 1933, 180 million pounds; 1934, 198 million pounds.
[g] Incomplete.

TABLE 11

Exports of Cottonseed by Major Exporting Countries[a]

Country	Cottonseed export, short tons										
	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944
Egypt	426,981	411,163	370,535	360,404	369,322	294,413	188,409	99,470	39,723	1	—
Brazil	81,404	121,018	90,336	72,470	67,913	61,071	20,749	2,878	—	—	—
Anglo-Egyptian Sudan	63,210	101,020	87,895	116,940	109,281	101,601	[b]	[b]	[b]	[b]	[b]
China	45,213	67,145	77,168	101,445	51,882	431	590	[b]	[b]	[b]	
Uganda	39,972	56,767	96,053	115,853	137,444	95,246	46,593	2,971	23,200	11	[b]
Peru	16,969	28,956	35,403	47,250	34,657	30,728	29,595	12,088	6,229	[c]	[c]
India[d]	712	818	10,083	5,609	521	2,073	151	246	535	1,594	476

[a] Official trade statistics. [b] Data not available. [c] No exports reported. [d] Year, beginning April 1.

TABLE 12

Imports of Cottonseed by Major Importing Countries[a]

Country	Cottonseed import, short tons										
	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944
United Kingdom	608,157	732,114	672,717	752,861	695,005	583,959	279,674	125,440	9,004	15,934	11,237
Japan	66,847	109,464	94,493	118,515	70,864	10,924	[b]	[b]	[b]	[b]	[b]
Chile	16,686	35,749	36,371	48,080	55,806	44,002	40,352	8,050	6,115	40	[b]
Denmark	10,496	1,633	8,601	5,516	12,822	8,921	8,788	—	—	[b]	[b]
Malta	6,568	8,178	7,363	5,200	5,536	[b]	[b]	[b]	[b]	[b]	[b]
Greece	2,268	2,596	726	205	9	20	—	[b]	[b]	[b]	[b]
Germany	916	285	3,040	9,320	8,166	5,942	2,151	4,382	5,629	317	[b]

[a] Official trade statistics. [b] Data not available.

domestically nor exported. Small amounts of Indian seed are utilized by the local oil industry and slightly larger amounts are shipped abroad, but by far the largest portion is consumed as cattle fodder.

Within the less important producing countries, Peru, Mexico, Argentina, and Iran have developed commercial crushing industries, but oil output in Uganda, Turkey, Chosen, and the Anglo-Egyptian Sudan is either negligible or nonexistent. Cottonseed oil is also processed in several noncotton-producing countries, with the United Kingdom far in the lead, followed by Japan, and Chile. Both the United Kingdom and Chile consume the major share of their oil output, exporting smaller quantities. In the case of Japan it appears that virtually the entire production is destined for foreign markets. By importing cottonseed and cottonseed oil from nearby Asiatic countries and shipping the oil and products containing oil to the United States, Japan increased the foreign exchange balances in this country which helped to pay for such imports as scrap iron and steel.

C. Foreign Trade

Unlike the other major oil bearing materials—copra, soybeans, flaxseed, and peanuts—the quantity of cottonseed entering foreign trade channels has never been significant in relation to total production. By far the bulk of all cottonseed produced is consumed within the country of origin. Among the more important producing nations, Egypt, Brazil, China, and India have exported the most sizable amounts of cottonseed, with the Anglo-Egyptian Sudan, Uganda, and Peru the only minor countries exporting in any quantity. Egypt, traditionally the number one exporter, is the only major producing nation whose overseas shipments during the immediate prewar period were comparable in size with amounts utilized domestically. However, even in Egypt exports were assuming less importance in relation to home use. During the years 1934–36, 45% of the entire Egyptian crop was shipped abroad; in the period 1937–39, only 39% of the total production left the country.

Of the other countries which ship appreciable percentages of the total world cottonseed exports, the Anglo-Egyptian Sudan and Uganda have virtually no domestic market for vegetable oil, and India's oil-producing facilities are largely undeveloped. Brazil, formerly one of the more important cottonseed exporting countries, has been utilizing increasing quantities of seed on the domestic market, and shipping less and less abroad. Peru's situation is very similar to that of Brazil. Wartime shortages of imported vegetable oils resulted in increased domestic crushing, while at the same time lost foreign markets for Peru's lint cotton have accounted for a curtailed cotton acreage, and a consequent decline in cottonseed exports.

With the exception of Peruvian and Chinese shipments, which moved chiefly to Chile and Japan, respectively, the United Kingdom received the bulk of all cottonseed exports. Of total 1937–39 cottonseed exports, nearly nine-tenths originated in Egypt, Brazil, the Anglo-Egyptian Sudan, Uganda, and India. Of this total 95% was destined for the United Kingdom. Emphasizing Britain's preferred position, British Empire countries alone—the Anglo-Egyptian Sudan, Uganda, and India—supplied approximately one-third of the total quantity of cottonseed entering world markets, and nearly all seed leaving these areas was shipped to the United Kingdom.

Japan, second most important importing nation in the prewar period, received the bulk of its incoming shipments from China and Manchukuo, with minor quantities originating in Iraq. Several Continental nations imported minor amounts of cottonseed prior to the war, and these quantities were utilized almost exclusively to satisfy domestic demand for cottonseed oil and cake. Among these countries Denmark, Germany, Greece, and Malta were the most important importers. Denmark's receipts are reported to have come from the United Kingdom; however, as the quantities were in line with Egypt's reported exports to Denmark, it appears that Egypt was the actual source of the Danish imports, which may have been trans-shipped from the United Kingdom. German receipts were supplied principally by Peru, Brazil, Nicaragua, and Egypt, while Greek imports originated mainly in the United States and Egypt, and Malta imported the bulk of its supply from Syria and Turkey.

Cottonseed oil is of even less significance in international trade than cottonseed. In the prewar period Brazil was the chief exporting nation, followed by the United Kingdom, China, Egypt, and Japan. The United States represented the most important market for these shipments, receiving 77% of all cottonseed oil leaving Brazil during the period 1937–39, 45% of the United Kingdom total, and a large share of the Japanese exports. These receipts into the world's largest producing country resulted from severe drought reduction in domestic fats and oils supplies. Egypt's shipments moved principally to the United Kingdom, and those of China were destined chiefly for Japan and the United States.

Among the other cottonseed products, cottonseed cake exports were most sizable in the prewar period. Principal shippers were Egypt, Brazil, and China, with the combined exports of these three countries averaging 537,000 tons annually. Smaller quantities were also exported from the United Kingdom, Japan, India, and the United States. The bulk of all protein-cake imports were received by the United Kingdom, Denmark, and Japan, with average 1936–39 receipts of these three countries comprising 670,000 tons.

TABLE 13

Exports of Cottonseed Oil by Major Exporting Countries[a]

Country	Cottonseed oil export, thousand pounds										
	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944
United Kingdom	29,872	46,715	36,928	57,202	23,395	10,099	676	192	6	—	—
United States	14,865	3,715	2,955	7,250	4,561	12,962	14,179	13,223	20,048	49,190	5,312
Egypt	7,343	32,163	26,619	23,712	15,622	28,920	20,648	14,167	7,965	64	43
Brazil	5,077	28,071	51,420	48,157	68,947	51,197	58,005	73,762	37,793	21,038	18,836
China	1,187	20,953	27,096	54,508	3,025	1,983	1,741	[b]	[b]	[b]	[b]
Japan	859	27,396	24,788	44,906	12,218	905	[b]	[b]	[b]	[b]	[b]
Argentina	2	536	55	[c]	—	4	2,582	15,527	16,374	44,238	31,838

[a] Official trade statistics. [b] Data not available. [c] Less than ½ the unit.

TABLE 14

Imports of Cottonseed Oil by Major Importing Countries[a]

Country	Cottonseed oil import, thousand pounds										
	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944
Germany	25,651	4,928	3,541	9,311	3,312	10,553	2,134	9,408	943	2	[b]
Canada	20,069	24,709	22,763	19,918	14,042	10,372	17,764	22,431	10,124	20,955	36,200
United States	9,157	166,687	127,787	194,031	77,500	29,454	12,031	23,660	8,372	12,196	10,052
United Kingdom	5,903	9,205	5,773	3,591	12,716	13,092	[c]	[c]	[c]	[c]	[c]
France	5,105	5,157	2,393	10	9	578	2,619	295	87	[b]	[b]
Japan	1,848	1,341	3,393	13,657	185	[d]	[b]	[b]	[b]	[b]	[b]
Cuba	[b]	6	1,313	2,855	3,305	262	1,455	123	1,021	[b]	[b]

[a] Official trade statistics. [b] Data not available. [c] Imports not shown separately. [d] Less than ½ the unit.

TABLE 15

Exports of Cottonseed Cake and Meal by Major Exporting Countries[a]

Country	Cottonseed cake and meal export, short tons										
	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944
Egypt	181,798	211,541	220,566	257,320	282,368	220,895	151,391	15,831	621	76	336
China	101,292	90,747	91,331	83,308	24,098	36,662	26,498	[b]	[b]	[b]	[b]
Brazil	61,797	96,215	169,670	227,147	244,413	229,768	157,192	35,230	280	17,543	57,110
Argentina	34,600	45,351	67,937	53,458	47,097	46,717	32,035	26,248	25,296	29,189	69,171
Japan	[c]	[c]	[c]	13,456	77	12	[b]	[b]	[b]	[b]	[b]
India	5,660	6,959	9,968	9,146	24,154	7,207	3,322	35	37	34	—
United Kingdom	2,126	6,931	6,387	9,568	1,700	[c]	[c]	[c]	[c]	[c]	[c]

[a] Official trade statistics. [b] Data not available. [c] Exports not shown separately.

TABLE 16

Imports of Cottonseed Cake by Major Importing Countries[a]

Country	Cottonseed cake import, short tons										
	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944
Denmark	236,569	255,357	311,704	334,825	384,651	352,604	125,056	543	—	[b]	[b]
United Kingdom	179,593	211,915	232,365	262,188	300,768	217,884	171,223	89,151	9,643	—	44,369
Japan	92,770	79,593	89,872	72,760	21,349	31,500	[b]	[b]	[b]	[b]	[b]

[a] Official trade statistics. [b] Data not available.

D. Future of the Industry

Expansion of cottonseed production is limited, in the main, by the possibilities for increasing lint cotton output. Among most major producing countries there is little indication of any marked expansion beyond the 1937–39 acreage level. In the United States, lack of a foreign market for lint cotton at U.S. price levels tends to discourage expansion. In both India and China domestic food requirements, and the high degree to which land is already under cultivation, preclude any appreciable increases. This is also true, to a lesser extent, of Egypt. There, however, additional land may be brought into cultivation through reclamation projects. In the case of the Soviet Union and Brazil, the only countries which showed a marked upward trend in cottonseed output during the period of the 'thirties, there is still the possibility of further increases. Such a development is almost certain to occur in the U.S.S.R. in line with the Soviet Union's self-sufficiency program relative to cotton. Brazilian cotton competes with coffee for both land and labor, and the relative prices of the two products on world markets will almost certainly be the decisive factor determining the size of the cotton crop.

Expansion is also feasible in several of the minor growing areas, particularly in Uganda, Turkey, and Iran. However, these areas supply such small quantities in relation to world production that even very sharp proportionate increases in cottonseed output from the minor producers would not result in any marked rise in the world total.

With regard to seed utilization within the producing countries, the United States is the only country where cottonseed crushing is carried on at optimum levels. Brazil and Egypt have expanded milling markedly within the past few years, and there are indications that this trend will continue. China's crushing is carried on to a large degree by primitive methods, and as China's industrialization program gains impetus it may extend to the cottonseed industry. There is also hope for improved and additional crushing in India, where a very high percentage of total seed output is currently wasted or fed whole to cattle. The U.S.S.R. in the past has made every effort to utilize all domestic resources to the full, and cottonseed oil production will undoubtedly increase in that country.

Among the minor producers, oil manufacturers in Peru and Mexico who have expanded their domestic markets during the war will certainly attempt to maintain these gains, and expand wherever possible. The cottonseed industries of Turkey, Iran, and Chosen are still largely undeveloped, and in the main it seems unlikely that there will be any great increase in crushing facilities until there is a stronger domestic demand for cottonseed products.

Commercial crushing is almost unknown in Uganda and the Anglo-

Egyptian Sudan, and with practically no local demand for cottonseed oil there is little possibility of a development of milling facilities.

II. Production and Consumption in the United States

The United States' position as the world's leading producer of cottonseed and cottonseed commodities dates back to the very earliest days of the industry. Commercial development of cottonseed was made possible by an American invention, Eli Whitney's cotton gin, in 1793. The eminence of the United States in this field has been maintained since that time.

A. Background

Expansion of the American industry proceeded slowly until 1881. At that time the cottonseed crush amounted to only 295,000 tons, no more than 5–10% of total seed production. The great improvement in transportation facilities was a prime factor in the rapid growth of the industry after that date. By 1891, 1 million tons of cottonseed were consumed by oil mills. This figure, doubling in 1897, and tripling by 1901, reached 4 million tons in 1910.

The United States' consumption of cottonseed has continued high, but fluctuates with the quantity of seed available. Seed output amounted to nearly 6 million tons in 1920–21, 6.2 million in 1930–31, 5.3 million in 1940–41, and 3.7 million in 1945–46. The major decline in 1945 cottonseed production, smallest since that of 1921–22, reflects the greatly reduced cotton crop, also the lowest since 1921–22, and the sharp decrease in cotton acreage harvested which was lower in 1945 than in any preceding year since 1885.

By far the greater part of the United States' cottonseed output is crushed domestically, with oil mills in this country consuming 78% of total cottonseed production during the period 1920–21 to 1944–45.

B. Cultivation

Cotton cultivation in the United States extends across the southern portion of the country, including 18 states.[1] Of the individual states, Texas is in the lead with regard to acreage, lint cotton production, and cottonseed output. In 1945 Texas cottonseed production comprised 741,000 tons, which was 20% of the United States' total. Four states, Texas, Mississippi, Arkansas, and Oklahoma, produced 60% of the 1945 crop, and 88% of the total is covered by including the output of Georgia, South Carolina, Tennessee, North Carolina, and Louisiana.

United States cotton acreage reached a peak of 44.6 million acres [2]

[1] Alabama, Arizona, Arkansas, California, Florida, Georgia, Illinois, Kentucky, Louisiana, Mississippi, Missouri, New Mexico, North Carolina, Oklahoma, South Carolina, Tennessee, Texas, and Virginia.

[2] Acreage harvested.

in 1926, and has declined more or less steadily since that date. The area harvested averaged 41.2 million acres for the five years, 1927–31, 29.9 million for 1932–36, and 25.5 million acres for 1937–41. A further decrease has been experienced in the past four years, with cotton acreage harvested falling from 22.6 million acres in 1942, to 17.7 million in 1945.

TABLE 17

United States Cotton and Cotton Products Statistics[a]

Crop year, beginning Aug. 1	Cotton acreage harvested, 1000 acres	Cotton production, 1000 bales of 500 pounds	Cottonseed production, 1000 tons	Cottonseed crushed 1000 tons	Crude cottonseed oil production, million pounds	Cottonseed cake and meal production, 1000 tons	Cottonseed hull production, 1000 tons	Cottonseed linters production, 1000 running bales
1930	42,444	13,932	6191	4715	1442	2165	1304	824
1931	38,704	17,096	7602	5328	1694	2401	1511	876
1932	35,891	13,002	5782	4621	1446	2093	1312	741
1933	29,383	13,047	5803	4157	1303	1889	1103	801
1934	26,866	9,637	4282	3550	1109	1614	913	805
1935	27,509	10,638	4729	3818	1164	1739	988	876
1936	29,755	12,399	5511	4498	1364	2031	1144	1127
1937	33,623	18,945	8426	6326	1961	2830	1626	1471
1938	24,248	11,944	5309	4471	1409	2023	1161	1113
1939	23,805	11,816	5259	4151	1325	1882	1055	1072
1940	23,861	12,565	5595	4398	1425	1954	1107	1208
1941	22,236	10,742	4788	4008	1250	1753	992	1184
1942	22,602	12,820	5717	4498	1401	1995	1085	1355
1943	21,652	11,429	4688	3955	1236	1834	927	1186
1944	20,009	12,230	4902	4253	1324	1954	984	1250
1945	17,059	9,015	3664	3262	1018	1434	783	989
1946	17,615	8,640	3513	3088	973	1362	727	991

[a] Acreage 1930–46 production cotton and cottonseed 1943–46 — U.S. Dept. Agr. All other figures — Bureau of the Census, U.S. Dept. Commerce.

Of the 1945 total, Texas led with 6 million acres harvested, followed by: Mississippi, 2.3 million; Arkansas, 1.6 million; Alabama, 1.4 million; Georgia, 1.3 million; Oklahoma, 1.2 million; and South Carolina, 1 million.

Cotton plantings in the United States range from small tenant farmer holdings of less than one acre to plantations containing thousands of acres. Of the 1.5 million farms growing cotton in 1941, 55% comprised 10 acres or less. As a further indication of the importance of the small producing unit, statistics for 1939 show that farms producing 10 or less bales of cotton covered 85% of the total farms growing cotton, 56% of the total acreage harvested, and 45% of the total cotton produced.

Planting seasons in the United States vary according to the region, with sowing beginning in February in the southernmost areas, and ending in May in the more northern states. Generally four months are required for cotton to mature. The harvest period begins in late July and is usually

completed by the end of December. After the raw cotton has been picked, it moves to gins where the lint cotton is separated from the cottonseed. In 1943 there were 12,000 cotton gins in the United States, of which 10,000 were active and 2,000 idle.

The number of gins has decreased markedly since 1902, when of a total of 33,000, 31,000 were operating. However, in 1902 an average of only 342 bales were ginned per active establishment, whereas in 1943 the average number ginned amounted to over a thousand bales. Texas leads other states with respect to the number of active gins, having 2,529 which produced 25% of the total seed output in 1943. Mississippi followed with 1,227 gins processing 16% of the national seed total, and Arkansas was in third place producing 10% of all seed, in 989 gins.

C. Production and Consumption of Cottonseed Products

The ginned cottonseed represents a considerable source of additional income to the cotton grower, and it is his chief source of cash income. During the ten-year period, 1934–43, the farm value of cottonseed amounted to 1.6 billion dollars, 21% of the 7.6 billion dollar farm value of lint cotton for the same years. The bulk of all cottonseed produced is purchased by the ginner who waits until he has accumulated a sufficient supply and then ships the seed by rail or truck to the crushing mills. In 1944, 394 cottonseed oil mills were operating in this country. Of this total, more than half, or 218 establishments, crushed between 5,000 and 20,000 tons of seed each, 43 crushed more than 20,000 tons, and 11, less than 1,000 tons. Texas was the leading state with 122 mills crushing 954,000 tons of seed.

In the season ending July 1, 1945, 1,250 thousand bales of linters were produced, compared with 1,186 thousand in the preceding year. Of the 1943–44 total, 84,000 bales comprised mill-run, 290,000 first-cut, and 812,000 second-cut. The output of hulls in the 1944–45 season amounted to 984,000 tons, compared with 927,000 in 1943–44.

Cottonseed oil, by far the most valuable of the cottonseed products, maintained its position as the number one source of domestic vegetable oils until 1944. In that year it was outranked by soybean oil, United States production of which had increased by 112%, as compared with 1941. Prior to the wartime increase in soybean plantings, output of cottonseed oil was more than double that of any of the other domestic vegetable oils. During the five-year period 1940–44, the average annual output of crude cottonseed oil, on a calendar year basis, amounted to 1.3 billion pounds. Consumption for the same years averaged nearly 1.4 billion pounds, the difference comprising the excess of imports over exports.

Cottonseed oil has long been established on the domestic market as a preferred vegetable oil. Approximately 90% of the total domestic output

is eventually consumed for edible purposes, as a salad oil, in shortenings, and in margarine. In addition to these major food uses, cottonseed oil is also utilized to a lesser extent in the packing of fish and cured meats. No more than 10% of the cottonseed oil produced in this country is consumed in inedible products. This amount is largely made up of the soapstock obtained in refining, which is utilized principally in soap.

During the calendar year 1944, 1,146 million pounds of cottonseed oil were consumed directly in manufactured products, of which 490 million was in shortenings, 215 million in margarine, 362 million in other edible products, 0.6 million in soap, and 5 million in other inedible products.

During the five years 1935–39, cottonseed oil comprised 41% of all fats and oils utilized in margarine manufacture, and 65% of all fats and oils consumed in the making of shortening. For the period 1940–44, these figures comprised 48 and 53%, respectively, with the decrease in shortening accounted for by the wartime increase in soybean oil utilization.

D. Foreign Trade

Prior to the imposition of import duties on coconut, cottonseed, peanut, and soybean oils by the emergency tariff act of 1921 and the so-called Fordney-McCumber tariff act of 1922, the United States exported very substantial quantities of both cottonseed and cottonseed oil.

TABLE 18

United States Foreign Trade in Cottonseed, Cottonseed Oil, and Cottonseed Cake and Meal[a]

Calendar year	Cottonseed, tons		Cottonseed oil, 1000 pounds		Cottonseed cake and meal, tons	
	Imports	Exports	Imports	Exports	Imports	Exports
1931	[b]	[b]	—	23,544	766	126,055
1932	—	[b]	—	55,768	490	100,390
1933	7	[b]	—	35,435	3,502	101,112
1934	—	[b]	9,157	14,865	22,446	20,491
1935	6	[b]	166,687	3,715	29,872	6,675
1936	[c]	[b]	127,787	2,955	13,685	6,110
1937	[b]	[b]	194,031	7,250	20,976	48,391
1938	[b]	[b]	77,500	4,561	3,295	47,237
1939	[c]	[b]	29,454	12,962	4,998	6,980
1940	[b]	[b]	12,031	14,179	39,650	1,156
1941	[b]	[b]	23,084	13,223	45,729	641
1942	[b]	2,621	8,372	20,048	39,650	1,118
1943	—	3,456	12,196	49,190	64,967	1,481
1944	34	2,112	4,353	5,312	90,952	108
1945	10	3,011	33,272	10,345	69,543	12
1946	—	4,606	—	6,101	38,983	20

[a] Bureau of the Census, U.S. Dept. Commerce.
[b] Not shown separately.
[c] Less than ½ the unit.

Since that time only very minor amounts of the total United States production of cottonseed products have entered foreign markets. From 1937 to 1939 the United States shipped an average of 2.3 million pounds of crude oil, principally to Canada; and 5.9 million pounds of refined oil, of which the major amounts moved to the Philippines, the Panama Canal Zone, Cuba, and Canada; and 21,800 tons of cake and meal, for which Denmark was the best customer.

Wartime 1942–44 shipments were at a higher level, and a considerable share of those totals was destined for Lend-Lease recipients. Mexico received the bulk of the annual average of 5.5 million pounds of seed which left this country; the United Kingdom and Canada imported the bulk of the crude oil exports, averaging 6 million pounds; and the U.S.S.R and the United Kingdom received most of the average of 18.8 million pounds of refined oil shipped each year. Cottonseed cake and meal exports declined during the war years, with the 1942–44 average comprising less than 1.1 thousand tons, destined principally for Canada.

In recent years, United States imports of cottonseed products have been at a higher level than outgoing shipments, but have never been significant in relation to total supplies. Receipts of cottonseed and crude cottonseed oil never reached sizable proportions, but in 1937–39 imports of refined oil averaged 93 million pounds; they declined to 8 million during the war period 1942–44, while incoming cake and meal shipments, which amounted to an average of only 19.6 millions pounds in the three years 1937–39, rose to a 130 million pound average for 1942–44. Brazil was the most important supplier of refined cottonseed oil for the years 1937–43, with less important shipments being received from Japan and the United Kingdom; in 1944 Argentina was the sole source of supply. A large proportion of the cake and meal imports in this country have also originated in Brazil; the major share of the remainder came from Mexico. While the United States is normally a substantial net exporter of cake and meal, the flow of these materials was reversed during the war years to provide protein feed for record numbers of livestock in this country.

E. Future of the Industry

During the past several years, cottonseed crushings have fluctuated from season to season, but the general trend has been downward. This movement is also reflected by the decrease in the number of cottonseed gins and oil mills. In the 1917–18 season 21,624 active gins and 763 oil mills were in operation. The number of these establishments declined to 14,863 and 557, respectively, in 1927–28, and to 12,838 and 466 in 1937–38. However, the decrease in the number of gins and oil mills has to a large degree been offset by the larger size and capacity of the units operating in 1937–38 compared with the earlier period. This consideration does not

apply to the decline since 1938. In the 1943–44 season, there were 394 oil mills crushing in the United States, a decline in number of 15% from the 1937–38 level. The number of gins operating in 1943–44 totaled 10,090, 2,748 establishments fewer than in 1937–38, and the average gin output of cotton for the same period declined from 1,442 to 1,103 bales.

It is clear that the cause of the 1938–1944 decrease has not been a slack market for cottonseed products. Demand for oil and cake and meal have been particularly strong throughout the war period, and during much of the time shortages of both commodities were experienced.

A general decline in cotton acreage and production, resulting from a variety of factors—including Federal Government programs to curtail plantings, the high price of United States cotton in relation to world markets, and wartime labor shortages—has been chiefly responsible for the decreased production of cottonseed commodities. No expansion in the United States cottonseed industry can occur until further quantities of seed are available. It has been suggested that one solution to the problem would be the growing of a type of cotton with a higher seed content, and experiments of this nature have been carried on in Texas, although not on a commercial scale.

As long as cotton production continues on a downward trend, the same general pattern can be expected to continue in the cottonseed products industry.

III. Production and Consumption in India

India ranks second among world cottonseed producing countries. Output during the 1944–45 season totaled 1.4 million tons, compared with the United States' production of 4.9 million for the same year. As a result of the wartime loss of foreign cotton markets in Japan and Europe, cotton acreage and consequently seed output declined considerably during the war years. The average cottonseed production in 1935–36 and 1937–38, amounted to 2.4 million tons, 71% higher than the 1944–45 figure.

A. Background

Commercial cotton production has been established in India for many centuries, and cotton cultivation has been constantly encouraged by the United Kingdom, anxious to obtain the bulk of the needs of the British textile industry from Empire sources.

B. Cultivation

Cotton acreage extends throughout most of India.[3] It is estimated that more than 10% of all cropped land in India is planted with cotton. Two

[3] Including the provinces of Punjab, Central Provinces, Berar, Bombay, Madras, Sind, and The United Provinces, and the states of Hyderabad, Baroda, Punjab, Bombay, Central India, and Rajputana.

main types are grown, Egyptian, which yields a black, lintless seed, and native and American Upland cotton, with similar white linted seed. Because of the different climates of the producing areas the sowing season extends from March through August. Approximately 10% of the total cottonseed production is utilized for seed, with plantings averaging 15 pounds per acre. Picking is usually completed in the three-month period, October to December.

After harvesting, the seed cotton is brought by bullock carts directly to the gins, if the farmers are located near a ginning center. Otherwise the cotton is sold in some instances in "market towns," where a cotton merchant purchases the seed cotton and resells to gins. Sometimes the gins have their own buyers in the market towns, and in other cases the agent operating either independently or on behalf of a gin travels from town to town. A special case is presented by the Bombay Presidency, where certain of the cotton growers have organized and produce pure strains of cotton. Marketing in this instance is done cooperatively, and often the pure-strain cotton brings a price higher than average levels.

C. Cottonseed Processing

The greater part of Indian cottonseed is consumed directly as a cattle feed. Crushing for oil, which has increased during the last fifteen years, still consumes a minor portion of the crop. In 1931 when total seed output was placed at 1.8 million tons, 1.4 million was utilized as a cattle feed, 224,000 tons was reserved for planting, 146,000 tons was exported, and only 22,000 tons—1.3% of the total production—was crushed for oil. By 1944 oil milling had increased markedly, and 336,000 tons of cottonseed were consumed by Indian oil processing plants: 112,000 by the two largest, 112,000 by so-called medium-size mills, and 112,000 by the small mills. Although it is known that there are 550 vegetable oil producing establishments in India, the number crushing cottonseed is not known.

The larger plants are equipped with modern machinery, including expellers or hydraulic presses. The principal establishments are located in Sind, Punjab, Bombay Presidency, Hyderabad, and Baroda. Small village or "ghanis" mills operate on an extremely primitive basis. Oil is produced by crushing the cottonseed with a pestle in a large wooden mortar. The pestle is made to revolve by means of a beam, hitched to two bullocks. Mills report an average oil yield of 15% for Indian cottonseed, but some estimates range up to 19%.

Although small amounts of cottonseed oil are exported, the bulk of the Indian production is consumed after hydrogenation in the domestic manufacture of vegetable ghee, a butterfat substitute. Cottonseed cake is also exported to some degree and the remainder utilized for food, as a fertilizer, and to a lesser extent as a cattle fodder. Use of cottonseed cake

as food is believed to be confined to India. The cake is ground to produce a flour, high in protein and fat, which may be used by itself or mixed with wheat flour.

Statistics relative to the total Indian production of cottonseed oil and cottonseed cake are not available.

D. Foreign Trade

India has never been a major exporter of cottonseed or cottonseed products. Cottonseed shipments for the period 1934–44 reached a peak of 10,000 tons in the year beginning April, 1936, and a low of 151 tons in 1940. Exports averaged 5,000 tons for the period 1937–39 and 850 tons for the years 1940–42, and amounted to 500 tons in 1943 and 1,200 tons in 1944. By far the major share of these shipments moved to the United Kingdom.

No exports of cottonseed oil were reported for 1941–44. During 1937, 1.5 million pounds of oil were shipped from India, principally to the Netherlands and Britain. Exports were much smaller for the 1938–40 period, averaging less than 9,000 pounds, of which the largest proportions were taken by the United Kingdom and "Other British Possessions."

During the decade of the 'thirties Indian shipments of cottonseed cake were fairly sizable, averaging 10,500 tons annually in 1934–39. They have declined considerably since that time, totaling only 35 tons in 1941, 37 tons in 1942, and 34 tons in 1943. Practically all cottonseed cake leaving India moves to the United Kingdom.

E. Future of the Industry

There is little likelihood of any appreciable expansion of Indian cotton acreage. The situation in India is comparable to that of China, where cropped acreage is already at a practical maximum and demand for food so high that further diversion of land to industrial crops is unlikely.

There is considerable possibility of a further expansion in oil crushing, however. Indian authorities are reported to be encouraging this move, as it is believed that the present widespread practice of feeding whole cottonseed to cattle is harmful. Postwar plans call for the erection of 27 additional vegetable ghee factories in India, and with these plants in operation domestic use of cottonseed oil could increase markedly. The market for ghee appears to be guaranteed, as India's output of butterfat is limited, and insufficient to supply domestic needs.

IV. Production and Consumption in the Soviet Union

The cottonseed production of the Soviet Union, which in the early 1930's was exceeded only by that of the United States, India and China, gradually increased during the prewar years. In 1937–38 an output of

2,017 thousand tons placed the U.S.S.R. third among producing nations. A peak production of 2,094 thousand tons was reached in 1938–39, with output declining since that date, largely as a result of necessary wartime diversion of acreage to food crops and German occupation of some of the growing sections. During 1941–42, the last year for which figures are available, 1,609 thousand tons of cottonseed were processed in the U.S.S.R. Unofficial estimates place the average 1941–45 cottonseed production at 1 million tons.

A. Background

Like nearly all other Eastern countries, Russia has grown cotton for many centuries. Earliest reports of cotton production are for the Central Asia region, still the most important cotton growing area. Peak cotton production for Tsarist Russia was attained in 1913, when 1,730 thousand acres were sown to cotton and 1.6 millions tons of unginned cotton were harvested.

The area cultivated did not expand markedly during the first decade after the Revolution, comprising 2.4 million acres in 1928, with the unginned cotton output for that year amounting to 1,808 thousand tons. From that date until the recent wartime interruption, however, there has been a marked increase in both acreage and output. By 1937 the Soviet Union was producing 10.3% of the world cotton supply, contrasted with less than 4% in 1929. Land sown to cotton for 1940, the latest available year, was placed at 5.2 million acres, an increase of 117% over the 1928 figure.

B. Cultivation

There are three main cotton growing areas [4] in the Soviet Union: Central Asia, Transcaucasia, and the so-called "New Region" which includes Stavropol, Crimea, and the Azov-Black Sea section. The Uzbek Republic of the Central Asia region is the most important cotton producer, which in 1938 accounted for 44% of total cotton acreage, and 55% of all cotton output. Since the cotton expansion program of the first five-year plan, cultivation has come almost entirely under government control. Whereas in 1927 individual peasant proprietors sowed 98% of the cotton area, by 1933 nearly 90% of this acreage was operated by collective and state farms, and only 9% by individual growers.

Collective and state farms utilize up-to-date cultivation methods. In 1937, 480 machine and tractor stations were servicing such farms with 400,000 tractors, 12,000 improved seeders, 10,000 cultivators, and a large number of picking machines.

[4] Comprising Georgia, Armenia, Azerbaijan in Transcaucasia; Turkmenistan, Uzbekistan, Tadzhikistan, Kazakistan, Kirghizia, Kara-Kalpak in Central Asia; and Stavropol, Crimea, Azov-Black Sea in the "New Region."

Seed is distributed to the planters by February 1, and planting usually continues through March. Cotton harvesting customarily begins in September, and picking, done for the most part by hand, is completed as soon as possible.

The Soviet Government owns all cotton gins and textile mills.

C. Cottonseed Processing

There is no recent information relative to utilization of cottonseed in the U.S.S.R. In 1934, 198 million pounds of cottonseed oil and 527 million pounds of cottonseed cake were produced. Output at this level represented gains of 183 and 86% respectively, over the 1927–28 figures.

In 1938, 1.2 billion pounds of vegetable oils were processed by government owned establishments, and 926 million pounds were produced in nongovernment plants. However, output statistics for individual oils are not available. As cottonseed is the second most important source of vegetable oil in the U.S.S.R., ranking after sunflower, and followed by linseed and hempseed, presumably cottonseed oil comprised a considerable share of the 1938 total.

During 1939, 75 government operated mills represented 46% of the total oil producing capacity of the Soviet Union. Nongovernment enterprises, including the so-called "cottage" industry, supplied the remainder. Presses of British, German, and United States manufacture were utilized in the government plants, and the solvent extraction method grew in importance.

Official information relative to cottonseed oil utilization is lacking, but undoubtedly a part of this output is consumed by the small but growing margarine industry. There is also some manufacture of shortening in Russia. Data regarding consumption of cottonseed cake, meal, and linters are not available.

D. Foreign Trade

Russia does not publish trade statistics showing countries of destination. In any case, exports of cottonseed products have been small. Cottonseed shipments totaled 42,000 tons in 1937, and 166 tons in 1938, with cottonseed oil exports amounting to 661,000 pounds during the earlier year, and no exports reported for 1938. Trade data show no imports of either commodity.

E. Future of the Industry

There is every likelihood that the Soviet Union will continue its cotton expansion program in the postwar period. By edict of November 11, 1945, the government established a Peoples' Commissariat of Industrial Crops Cultivation of the U.S.S.R., in charge of such crops as cotton, flax, hemp, tobacco, and tea. The Commissariat will meet some handicaps in ex-

panding acreage beyond the immediate prewar level, as most new land which can be planted to cotton will require extensive irrigation facilities. However, this problem has been faced in a great many of the regions already growing cotton, and it is doubtful that it will prove a sufficient difficulty to prevent any planned increase.

There will certainly be a market within the U.S.S.R. for any additional supplies of cottonseed. The prewar annual per capita consumption of fats and oils in the Soviet Union totaled only 16.5 pounds. Consumption was maintained at approximately the same level for unoccupied Russia during 1943–44, largely because of imports from the United States. With the withdrawal of lend-lease arrangements, United States' shipments to the U.S.S.R. contracted sharply, and because of the wartime decrease in hog numbers, Soviet fat output is not presently sufficient to maintain consumption at normal levels. Therefore, any increase in cottonseed production will tend to be consumed on the home market.

V. Production and Consumption in China

Although the Chinese cotton industry has been established for many centuries, and China is ranked as one of the world's most important producers, official statistical data covering her output of cottonseed and cottonseed oil are not available. Unofficial sources placed Chinese seed production third only to that of the United States and India until 1937–38, when output by the U.S.S.R. exceeded that of China. Later estimates indicate that Russia continued to produce at a higher level than China, and world harvest figures show that beginning with the 1939–40 season Brazil's crop also outranked that of China.

A. Background

Chinese cottonseed production, which averaged 1.3 million tons for the period 1923–33, and amounted to 1.5 million and 1.6 million tons, respectively, for 1933–34, and 1937–38, does not reflect the expansion in cotton plantings that occurred during the period 1932–37. In contrast, lint cotton output does indicate this increase. During the years 1920–31, there was no marked development of the domestic industry, with the area planted averaging 5.6 million acres, and the lint cotton output, 2.5 million bales. In 1932, when a total of 6.8 million acres were planted, lint cotton production showed a corresponding rise to 3.0 million bales. Expansion continued until the outbreak of the Sino-Japanese War of 1937, with acreage reaching a peak of 9.3 million acres in 1937, and with a record lint cotton production of 3.9 million bales reported in 1936. This increase of more than 3 million acres over the period 1932–37 represents a very significant development in Chinese industry. As less than 5% of the expansion in cotton acreage took place on new land, almost the entire increment

in cotton acreage resulted in a comparable decrease in the area planted in food crops. Intensive land cultivation is practiced in China, and very little soil lies fallow. It is estimated that through decreasing the area devoted to food crops by 3 million acres, food supplies sufficient to feed 7 million people were lost. The Chinese Government encouraged the expansion of domestic cotton production, largely as a measure to conserve foreign exchange. In order to protect the market for the local cotton output, import duties on raw cotton, yarn, and piece goods were sharply increased, and by 1936 China had become largely self-sufficient with regard to cotton, and the domestic product had almost entirely replaced former cotton imports.

Japanese aggression brought the cotton industry's expansion to a standstill. Data covering the war years are lacking or are extremely unreliable, but a preliminary estimate of 1944 acreage [5] indicates less than 4.4 million acres planted to cotton, less than in any of the years 1920–41. Although acreage statistics are probably not completely accurate, as there is some cotton production throughout China, they do cover adequately plantings in the major growing areas—the Yangtze valley and North China.[6]

B. Cultivation

Climate, soil, and crop systems differ considerably in the above-mentioned two sections of China. In the Yangtze valley, which is in approximately the same latitude as southern Georgia, a second crop, in addition to cotton, is grown regularly each year. In the North China region, with approximately the same latitude as the cotton growing areas of North Carolina and southern Virginia, one crop of cotton a year is harvested from the land, and no other crops are grown in conjunction with cotton. The rotation system is generally practiced, usually in 2- or 3-year cycles. Acreage expansion during the 1932–37 period occurred largely in North China.

Although situated in climatically different areas, planting of cottonseed usually occurs during May in both the Yangtze valley and in North China. Often in the valley region cottonseed is broadcast in the wheat and barley crops, and by the time late May or early June harvests of the grain crops are completed, the cotton plants are from 1 to 3 inches

[5] "World Cotton Production Lower in 1945," in *Foreign Crops and Markets,* U.S. Dept. Agr., **51,** No. 22, 308 (1945).

[6] Principal growing regions, Yangtze River area: the Nantungchow district of Kiangsu Province; the south bank of the Yangtze; the territory surrounding Shanghai; the area west and northwest of Hankow in Hupeh Province; Chekiang Province on the south bank of Hangchow. Minor producing areas: Anhwei, Kiangsi, Hunan, and Szechwan Provinces. Yellow River valley area: southern Hupeh, northwest Shantung; northern and northwestern Honan, Southern Shansi, and Eastern Shensi. Minor producing areas: Shantung Province, and the Tientsin area.

high. North China cotton is spring plowed and harrowed, with the seed being planted in rows, by hand. Fertilization is carried on extensively throughout China. Manure, mud, and ashes are most commonly used on cotton; oilseed cake is used less frequently. Upon reaching maturity, cotton is picked by all members of the Chinese farming family. Picking begins first, usually by mid-August, in the Chekiang province, and continues until early October in North China. Several pickings are made throughout the season, and very little cotton is lost.

During the fall and winter months when demand for farm labor is at a low ebb, the seed cotton is ginned in the home with spike gins operated by foot. This practice is widespread; however, some farmers located near cotton centers sell seed cotton directly to a central gin.

C. Cottonseed Processing

China produces a variety of lint cottons, and consequently of cottonseed types. Seed varieties are classified according to color: green, black, and white. Green seed, which has the highest oil content, is harvested largely from the old salt beds on the coastal area between the outlets of the Yangtze and Yellow rivers. This type of seed yields approximately 10% of oil, with the black and white varieties yielding about 9.5% and 8–9%, respectively.

The bulk of the cottonseed produced is utilized domestically. Seed is crushed in the heavier producing areas, with the oil being used principally for cooking purposes, and to a lesser extent as an illuminant. The chief outlet for cottonseed cake and meal is as a fertilizer for rice and wheat; smaller quantities are utilized as a livestock feed.

Although a large amount of seed is probably crushed directly by farmers, using primitive crushing equipment, there are also several large oil mills in Shanghai and Hankow, as well as other commercial establishments located in the growing areas. Usually the pressing season begins in September and continues through April if the seed supply is sufficient to maintain operations.

D. Foreign Trade

Japan provided the major market for China's exports of cottonseed and cottonseed products in the prewar period. During the years 1934–38, cottonseed shipments averaged 69,000 tons; cottonseed oil, 21 million pounds; and cottonseed cake and meal, 78,000 tons.

E. Future of the Industry

As in other cotton-producing countries, consumption and exports of cottonseed in China are determined by the demand for lint cotton and not by seed and oil requirements *per se*.

Currently, as a result of World War II, Chinese cotton and cottonseed output is low. There are many indications, however, that production will increase at least to the 1935–37 level in the postwar period. The National Government fostered expansion to meet domestic needs in the earlier period, and will be likely to adopt a similar policy as the political situation becomes more stable.

Several factors tend to limit expansion of the Chinese crop beyond the limits of the 1935–37 acreage. Land cultivation is already intensive and possibilities of expanding cotton acreage on areas not being utilized for other crops is unlikely. Nearly all such land is either unsuitable for cotton production or requires considerable capital expenditure for reclamation, drainage, or irrigation projects.

Estimates indicate that approximately 90% of all land farmed is utilized for food production; China's dense population requires this large scale output. Any diversion of food-producing areas to the cultivation of cotton will be largely dependent upon the relative prices of food crops and cotton. Whereas cotton prices are largely determined by world trends, food prices are more responsive to the level of Chinese output. Failures of food crops bring about very high food prices and farmers shift plantings from any lower priced commodity.

This situation would be considerably altered if there were an improvement in China's transportation facilities. Food supplies could then be channeled from surplus areas to those provinces in which the supply is scant. At the same time marketing costs of cotton would be reduced. Presently, however, there appears to be little likelihood of any considerable expansion in cotton acreage beyond the 1935–36 level.

VI. Consumption and Production in Brazil

Brazil, the fourth ranking cottonseed producer since 1939, when approximately 1.1 million tons of seed were processed, expanded production rapidly during the period 1933–1944. A peak production of nearly 1.3 million tons of cottonseed was reached in 1944. A severe drought curtailed the 1945 output, which is now placed at 724,000 tons.

A. Background

The earliest European explorers found cotton growing in Brazil, both in the northern part of the country, and in what is now the state of São Paulo. Colonists continued cultivation, and by the middle of the eighteenth century cotton had become an export crop of considerable importance. Production rose sharply in the early 1900's and has shown a slight upward trend from that time on. A very marked expansion occurred in 1933; cotton output in that season totaled more than 1 million bales, compared with 455,000 for the preceding year. Reflecting this increase, cottonseed pro-

duction rose from 389,000 tons in 1933 to 732,000 tons in 1934, an increase of 88%.

Brazil has two cotton-producing regions: the northeast and the south.[7] Methods of cultivation, production, plant types, planting and harvest times, and seed utilization are at distinct variance in these two areas.

B. Cultivation in São Paulo

São Paulo, the southern cotton center, and by far the most important producing state, has expanded its acreage markedly since 1932. In that year approximately 0.5 million acres were planted to cotton, compared with the record 1943 sowing of 4.5 million acres. A system of large land holdings is predominant in São Paulo, and the bulk of the cotton crop is produced by cash or share tenants. There has been an increase during recent years in the number of small farm owners, but this group does not account for more than 10–15% of the total area in cotton. Immigrant labor provides the main source of cotton plantation workers, approximately 40% of which are of Japanese origin. Planting is carried on during the months of September, October, and November; picking, beginning the following March, is usually completed by June. A system of state distribution of seed has proved highly successful in São Paulo, with the cotton type steadily improving and plant disease being controlled to a large degree. The lint cotton produced is similar to the American Upland type and competes with the United States variety on world markets. São Paulo is in a preferred position, compared with other Brazilian cotton-producing states, as soil and climate are more favorable and the industrious labor force drawn from a relatively dense population operates more efficiently than the less aggressive rural labor of the northeast.

Industrialization of the cottonseed industry has also advanced much further in São Paulo than elsewhere in Brazil. In 1944, 82 gins were owned by the cottonseed oil mills, in addition to establishments owned by ginners under contracts with the mills, and other gins operated by large plantation owners. Tenants on the large plantations must sell their cotton to the landowner at current market prices.

C. Cottonseed Processing in São Paulo

São Paulo's total output of cottonseed oil in 1944 is placed at 193 million pounds. This oil is produced in modern mills, utilizing relatively up-to-date equipment. Of the 23 establishments operating in 1944, 21 used hydraulic presses, and the other 2, screw presses. Some machinery is of Brazilian or German manufacture, but the bulk is of United States origin.

[7] Includes states of Pará, Maranhao, Piaui, Ceará, Rio Grande do Norte, Parahiba, Pernambuco, Algoas, Sergipe, Amazonas, Esperito Santo and Bahia in the northeast, and São Paulo, Minas Gerais, Rio de Janeiro, Paraná, Matto Grosso, and Goiaz in the south.

Normally the crushing season extends from May through March, and it is common practice for the mills to operate on a 24-hour schedule. The total capacity is estimated at 900,000 to 1 million tons of seed, with potential output placed at 190 to 210 million pounds of oil. Refining capacity estimates run as high as 350 million pounds. Actual oil production from the 1945 cottonseed output will run considerably below capacity, being expected, because of crop failure, to amount to less than 80 million pounds. Production of oilcake and meal will also be considerably lower in 1945, with the total now placed at 126,000 tons compared with 273,000 in the preceding year.

Statistics covering the production of linters and hulls are not compiled, but it is estimated that one ton of cottonseed yields 260 pounds of oil, 800 pounds of cake and meal, 860 pounds of hulls, and 80 pounds of linters.

Consumption of domestic cottonseed oil in São Paulo has increased markedly since the depression years of the early 1930's. Depreciation of the milreis in relation to foreign currency at that time tended to discourage imports of foreign vegetable oils. Receipts of olive oil, the principal edible oil on the São Paulo market, declined from 4,601 metric tons in 1930 to 1,562 metric tons in 1931, and averaged 2,301 tons for the years 1932–35. These imports, which originated principally in Italy, Portugal, and Spain, were further curtailed as a result of the war. Increased use of locally produced oil has more than filled this gap. São Paulo consumption of domestic cottonseed oil, placed at no more than 40 million pounds in 1934, totaled nearly 80 million pounds in 1944, and 95 million pounds in 1945. The total Brazilian consumption of cottonseed oil exceeded 150 million pounds in both 1944 and 1945. Local consumption of cottonseed cake and meal has also increased markedly, almost entirely as a result of World War II, which cut off Brazil from her Continental foreign markets.

Large quantities of cake have been used for fuel by railroads to replace former coal imports, and considerable amounts have also been utilized as cattle feed. São Paulo cattlemen were reluctant to try cottonseed cake and meal, but because of government encouragement and the low cost of this product in comparison with other feeds, increasing quantities have been consumed, particularly during the dry winter months when pasture conditions are poor.

D. Cultivation in Northeast Brazil

Information regarding cotton culture in the northeastern states is not as readily available as in São Paulo. In recent years the importance of this area has been declining, although until 1930 the northeastern states contributed the major share of the total cottonseed output. In 1943 the Brazilian Government estimated that the combined seed output of the northeast region comprised slightly more than 34% of the total for all

Brazil, with oil production for the area placed at approximately 12% of the total.

Development of cotton culture in these states has been handicapped by periodic droughts, scanty transportation facilities, and the lack of a modern textile industry.

In general the Brazilian Government's program of seed distribution has been less successful in the North. There is no uniform type of cotton grown, although tree cotton is most common. This variety requires little cultivation, the trees producing during a period of three to seven years, and sometimes yielding for a much longer period. Where annual cotton is sown, planting occurs in the January–June months, followed by an August–January harvest. The plantation system of São Paulo is not established in the northeastern states, and production on small plots by individual farmers is the rule.

E. Cottonseed Processing in Northeast Brazil

Total cottonseed production in the northeast region amounted to 233,000 tons in 1944, and oil output for that year was placed at approximately 29 million pounds. Potential cottonseed oil production for the thirteen mills operating in the Pernambuco Consular district (comprising the states of Ceará, Rio Grande do Norte, Parahaiba, Pernambuco, and Algoas) in 1939 amounted to 65 to 110 million pounds, but consumption of seed for cattle feed and inadequate transportation facilities prevented crushing at this level. Later information relative to Ceará only, shows ten mills crushing cottonseed in that state, but no capacity figures are reported.

F. Foreign Trade

Brazilian exports of cottonseed and cottonseed products increased sharply during the decade of the 'thirties. In 1933 shipments of cottonseed amounted to less than 10,000 tons, and oil exports were less than 60 thousand pounds. By 1935, the peak year for seed exports, more than 121 thousand tons of cottonseed was shipped abroad, in addition to 28 million pounds of oil. Exports of cottonseed declined after that date, as a result of increased domestic crushing. Oil exports, however, continued to rise until 1941, when a record 74 million pounds left the country. Since that date, largely because of increased domestic demand, oil exports have been at a considerably lower level, comprising 38 million pounds in 1942, 21 million in 1943, and 19 million pounds in 1944, compared with the 1936–40 average of 55 million pounds. Brazilians were somewhat slow to accept cottonseed oil as an olive oil substitute. However, by 1942 domestic cottonseed oil had entirely supplanted European olive oil. In addition to

consumption as a cooking and salad oil, large quantities of cottonseed oil are used in soap and margarine manufacture.

Before World War II Great Britain provided the major foreign market for Brazil's cottonseed shipments, receiving 94% of all exports for the period 1937–39. During these years the United States, despite a large domestic production, received the bulk of all cottonseed oil leaving Brazil. This position was maintained until 1943, when Canada supplanted the United States as the number one foreign oil market. Exports to the United States in that year comprised only 661,000 pounds compared with more than 30 million in 1942.

A further wartime development was the loss of Denmark and Germany as outlets for cottonseed cake and meal shipments. During the period 1936–39, of a total of 871,000 tons of Brazilian cottonseed cake and meal shipped, 478,000 tons or 51% was destined for Denmark and 332,000 or 38%, for Germany. In the period immediately succeeding the outbreak of war, Brazil was faced with a difficult problem of disposal, but rising domestic demand for cake and meal as a cattle feed, fuel, and to a lesser extent as a fertilizer, gradually absorbed this surplus.

G. Future of Cottonseed in Brazil

Maintenance of cottonseed and cottonseed oil production in Brazil at the level of the past five years or a further expansion is dependent upon the state of the cotton industry. All indications are that cotton cultivation in northeast Brazil has reached its peak, and has been on the downgrade for the past several years. Average lint cotton production in northeastern Brazil for the years 1941–45 amounted to 108,000 tons, a 32% decline from the 1940 figure of 159,000, and approximately the same as the 1931–35 average of 109,000 tons.

However, because of the increasing output from São Paulo, the total Brazilian production shows an actual increase of 191% for the period 1941–45 as compared with 1931–36. Brazil's highly protected domestic textile industry will no doubt continue to expand and consume increasing quantities of cotton for sale at home. However, a continuance of cotton crops comparable with those of the past decade or any further expansion depends upon favorable overseas markets for Brazil's cotton. Traditionally, cotton competes for both land and labor with coffee, São Paulo's major industry and Brazil's principal export crop. Expansion of cotton acreage in São Paulo reflects the consistent high price premium of cotton over coffee. During 1901–1944, the average kilogram value of Brazilian coffee exports exceeded those of cotton in only four years, 1912, 1926, 1929, and 1942. This factor has not resulted in any large scale diversion of capital and labor already established in the coffee industry, as coffee plantations represent a long-time investment. However it can be expected

that new land, capital, and labor will move to cotton rather than coffee as long as the price spread continues. In addition, cotton may replace old coffee areas on coffee farms and may be grown in addition to coffee whenever coffee prices are low, although this tendency is somewhat checked by the fact that cotton and coffee harvests coincide—and unless an unusually large labor force is available, might prove impractical.

It appears that as long as cotton remains high-priced in relation to coffee there will be an expansion of cotton growing in São Paulo. Whether or not Brazil can continue to increase output and consumption of cottonseed products, is more difficult to predict. Presently, at least partially because of wartime shortages, Brazil's domestic market is absorbing a major share of its cottonseed oil and cake and meal output. When imported olive oil is again readily available there may be a return to this commodity, and it is almost certain that foreign coal will replace cottonseed cake and meal as a fuel. In the immediate postwar years Brazil will find a ready market in the United States or Europe for its oil shipments, and cottonseed cake and meal will be in strong demand on the Continent. Whether or not these markets are maintained, from a long-range point of view, will depend mainly upon the price of these commodities in relation to competing oils and raw materials from the Far East.

VII. Production and Consumption in Egypt

Until shipments were interrupted as a result of World War II, Egypt traditionally represented the world's most important source of cottonseed exports. Among world producers, Egypt's cottonseed output has long been exceeded by the production of the United States, India, China, and the U.S.S.R., and since 1934–35 the Brazilian crop has outranked that of Egypt. Nevertheless, Egypt continued to maintain its position as the number-one exporter until 1942. Egyptian cottonseed shipments were drastically curtailed as a result of the war, and were actually banned by official decree of March, 1942.

A. Background

Established for well over a century, cotton is by far Egypt's most important crop, occupying 22% of all cultivated acreage (1934–38 average). Combined with shipments of cottonseed and cottonseed cake, cotton represented nearly 91% of the total value of all commodities exported during the period 1936–38.

Early Egyptian crop statistics show 200 bales of cotton produced in 1820, with production rising slowly until the Civil War period in the United States. Great impetus was given Egypt's cotton industry as a result of the blockade of American cotton shipments. By 1861 the Egyptian cotton harvest amounted to 150,000 bales; it increased to 414,000 bales by

1863, and totaled 622,000 in 1879. Production continued to increase until the World War I, with the 1913 crop placed at 1.6 million bales. Since that time the cotton crop has fluctuated from year to year, and no clear-cut trend has been established.

B. Cultivation

Like that of other agricultural crops, cotton cultivation [8] is confined to the Nile Delta in lower Egypt and the Valley of the Nile in middle and upper Egypt. Planting occurs during the months of February–April and the harvest extends through the August–October period. Because of the temperate climate, crops may be grown year-round; but rotation is generally practiced and usually no one crop is grown on the same land during two consecutive years. Plantings vary according to the particular conditions of the area. Under one system cotton is sown in March, wheat is planted in November or December, corn is sown in July, with berseem [9] being interplanted in November, and cotton is again sown in March. Various substitutions may occur, but as demand for both food and cash crops is strong, no land is allowed to lie fallow for any considerable period.

Cotton cultivation is carried on by all types of growers, including small farmers tilling less than one acre and owners of very large plantations. No difficulty is experienced in securing sufficient agricultural labor, except in the cotton picking season on the basin lands of upper Egypt.

C. Cottonseed Processing

Crushing of cottonseed by domestic Egyptian mills has increased substantially since World War I. Reports show that an average of 138,000 tons of seed was consumed by the crushing industry during the period 1914–15 to 1917–18. In the years 1941–42 to 1943–44, this figure had risen to 441,000 tons.

As output of cottonseed oil has increased, production has tended to be concentrated in a comparatively few establishments. In 1937, five mills accounted for 80% of the entire oil output, estimated at 132 million pounds, and the two largest mills accounted for 60% of the total.

Of the cottonseed processing establishments operating in 1937, it is reported that twelve were gradually modernizing their equipment. Cage presses, and in some cases, up-to-date continuous presses had replaced former open presses. Automatic filter presses were in use for filtering and refining, with some mills purchasing this type of equipment from United States manufacturers.

Capacity oil output was placed at 220 million pounds in 1937, com-

[8] In the provinces of Beheira, Gharbija, Dagahliya, Menufija, Zalyubuja, and Shargiya in lower Egypt; Beni-Suef, Faiyum, Giza, and Minya in middle Egypt; and Aswan, Asyut, Girga, and Zena in upper Egypt.

[9] Berseem is a winter annual clover, a highly important cattle feed in Egypt.

pared with an estimated actual output of 132 million pounds. The capacity figure is based on a 24-hour day for the October–June crushing season. Egypt's largest mills are in Alexandria, with less important plants being located in Assuit, Cairo, Mit Ghamr, Tanta, and Delta Barrage. Of the three types of cottonseed oil produced by the Egyptian industry, *English, Sultani,* and *French,* more than 80% is accounted for by the English type. Oil of this grade is sold on the domestic market both for edible purposes and for use in soap manufacture. "English" oil was also the type most frequently exported in the prewar period. "English" oil is produced by treating the crude oil with caustic soda solution. After further refining by decolorizing and deodorizing, it is sold under the name "Sultani," and is then utilized exclusively as an edible oil. The greatest premium is attached to the "French" grade of oil, a completely refined product destearinized by a process of refrigeration and filtration. The residue from caustic refining is used in the manufacture of cheap laundry soap or for further manufacture into fatty acids.

During the prewar period it is estimated that the Egyptian cottonseed oil industry produced 88 million pounds of oil annually for domestic consumption and varying amounts for export, with average 1935–38 shipments to foreign markets comprising slightly over 12 million pounds.

Wartime conditions brought about a sharp rise in domestic consumption and the termination of all cottonseed oil exports. Use of locally manufactured oil is placed at 195 million pounds in 1941–42, 155 million pounds in 1942–43, and 123 million pounds in 1943–44. The two earlier higher figures are accounted for by the fact that the consumption statistics for that period included use by the British and Allied armed forces in Egypt, regarding which no data are available. During 1943–44 the oil used was supplied by imported seed crushed by the British authorities, for which estimates have not been provided.

Prior to the war, oilcake output averaged approximately 216,000 tons. The production of cake amounted to 300,000 tons in 1942–43, 220,000 tons in 1943–44, and 350,000 tons in 1944–45. In normal times the bulk of the cottonseed cake is exported. Average shipments for 1935–38 comprised 243,000 tons. During the war period, however, domestic utilization rose sharply, absorbing the entire output in 1942–43 and 1943–44. In both years, approximately 15% was used as a fertilizer, and the remainder was consumed almost entirely as a fuel, with only very minor quantities being used as a cattle feed.

D. Foreign Trade

1. Cottonseed

Egypt's prewar position as the world's most important supplier of cottonseed was established early in the twentieth century. Average annual

shipments for the ten-year period of 1914–15 to 1924–25 amounted to 320,000 tons, and exports for the period 1924–34 averaged 350,000 tons. Britain received by far the major share of these shipments, remaining the chief importer through 1942. Cottonseed shipments from Egypt averaged better than 340,000 tons in the years 1937–39, and of this total 317,000 tons or 93% was destined for the United Kingdom. Exports declined from 370,000 tons in 1938 to 295,000 tons in 1939, and decreased even more sharply in the succeeding war years, amounting to 189,000 tons in 1940, 100,000 tons in 1941, and 40,000 tons in 1942. Exports of cottonseed, cottonseed oil, and cottonseed cake were banned by the Egyptian Government in *Arreté No. 39* of *Journal Officiel No. 58* of March, 1942, and any subsequent shipments comprised only minor quantities.

2. Cottonseed Oil

During the early stages of development of the cottonseed oil industry the bulk of the oil output was exported. As early as 1923 shipments of cottonseed oil totaled 25 million pounds, and average yearly exports in the period 1927–31 comprised 23 million pounds. A decline in this figure to 14 million pounds for 1930–34 reflects the loss of the British market, which had received a large share of outgoing shipments. Under the British Import Duties Act of 1932 cottonseed oil imports of non-Empire origin were taxed at a rate of 10% *ad valorem*. Egypt's exports declined from 26 million pounds in 1929 (of which more than 50% went to the United Kingdom) to 4 million pounds in 1933, with little better than 1 million pounds destined for Great Britain. Shipments continued low in 1934, but improved markedly after that date. Average exports in 1935–39 amounted to 25 million pounds. During this period the United States, Germany, and the United Kingdom received the bulk of Egypt's shipments, but no one market furnished a major outlet comparable to the United Kingdom in earlier years.

With the outbreak of war, cottonseed oil exports were banned by the Egyptian Government. Because of the importance of the foreign market, however, this restriction was removed in November of 1939. In November of 1941 export of cottonseed oil without specific authorization was again prohibited and this ban was continued by official order of March, 1942. In April, 1945 the restriction was still in effect.

Cottonseed oil exports amounted to 21 million pounds in 1940, 14 million pounds in 1941, and 8 million pounds in 1942. After that time only small amounts of cottonseed oil moved out; the production and distribution is closely regulated by the Government. A system of card rationing of cottonseed oil for food is in force and industrial users are also rationed. During the entire period from 1943 through 1945 less than one million pounds of cottonseed oil were exported.

3. Cottonseed Cake

In prewar years practically the entire Egyptian production of cottonseed cake, which averaged approximately 250,000 tons, was exported. Shipments moved principally to the United Kingdom and northern Europe. In 1940, the last year in which sizable exports of cottonseed cake are reported, 151,000 tons left the country, with the United Kingdom receiving 140,000 tons.

E. Future of the Industry

Because of the importance of cotton in the Egyptian economy, there is little likelihood of any marked or continued decline in cotton cultivation in the postwar period. At the same time, any appreciable expansion beyond the 1.8 million acre average of 1935–39 would require reclamation of waste land. Presently it appears that unless there is some major shift in the cotton market, output of cottonseed in Egypt will continue at approximately the 1934–35 to 1937–38 average of 875,000 tons.

More consideration is required with regard to the cottonseed oil situation. Output at the 1944–45 level of 140 million pounds would require a domestic market for 115 million pounds of cottonseed oil, if exports are resumed at the average 1935–39 annual rate of 25 million pounds. Domestic consumption at this level would be considerably in excess of the average yearly prewar use of 88 million pounds, but much less than wartime utilization which, excluding use by the British Army, amounted to an estimated 163 million pounds a year.

If Egyptian domestic cottonseed oil is able to compete with foreign oils formerly imported for edible consumption and for use in the soap kettle, there is a strong likelihood that postwar cottonseed crushing will continue at wartime levels, or show a gradual upward trend from these levels.

VIII. Production and Consumption in Other Areas

By far the greater part of the world's cottonseed output is provided by the countries already discussed. Production by each of the remaining areas is not significant when considered individually, and even the combined total output of these areas does not make a sizable addition to over-all cottonseed supplies. League of Nations statistics[10] show that in the 1940–41 season, the last year for which figures are available from all countries, the combined production of Uganda, Peru, Mexico, Turkey, Iran, Chosen, and the Anglo-Egyptian Sudan amounted to 975,000 tons, 6% of the world total for that year.

[10] *Statistical Year-Book of the League of Nations, 1943,* printed in the United States by Trenton Printing Co., p. 115.

A. Turkey

Production of cottonseed in Turkey totaled 165,000 tons in 1943, which was considerably lower than the 1939 peak of 189,000, but a sharp rise from the 1942 figure of 128,000 tons.

Cotton, introduced into Turkey in the early nineteenth century, has experienced wide variations in output since that time. Cultivation expanded greatly during the American Civil War and contracted greatly after that time. Again in 1913 cotton production was on the upgrade, only to be set back by World War I and the Greco-Turkish conflict of 1919–22. In 1913 the cotton crop was estimated at 150,000 bales, while 1923–25 crops averaged only 72,000 bales. In 1930 the Turkish Government instituted a program to encourage cotton production, both for home consumption and export, and acreage increased from the 1923–25 average of 400,000 acres to 700,000 in the 1936–38 period. At the same time both production and yields also increased. This most recent expansion was checked as a result of the wartime loss of foreign markets for lint cotton. During the years 1936–38 Germany and Italy absorbed 73% of Turkey's total cotton shipments. The reduced cotton crops are reflected in decreasing production of cottonseed. Seed output declined from 189,000 tons in 1939, to 172,000 in 1940, and 126,000 tons in 1941. The latter figure was the lowest in recent years, with the output rising to 128,000 tons in 1942 and 165,000 tons in 1943. Statistics for later years are not available.

The principal cotton-growing area of Turkey is in South and West Anatolia, located in Asiatic Turkey. Cultivation methods are primitive. Cotton planting usually commences in early March, the seed being sown broadcast. The seeds are then covered by means of a steel-pointed wooden plow, and a log drag is pulled by oxen. Nomadic tribes supply the bulk of the labor utilized in sowing, and often no further attention is given the crop until the August–September harvest period. Since 1942 the Turkish Government has purchased the entire crop after ginning, and during the war period the Government controlled all phases of the cotton industry. As a rule, the small peasant growers retain their cottonseed after it has been ginned either in commercial ginneries by roller gins, or hand-separated at home. After requirements for planting have been set aside, the remainder of the seed is crushed by primitive methods and utilized as a livestock feed. The actual quantity of seed consumed commercially is not known, as no data regarding oil production are available. In 1935, six oil mills with a combined capacity of 12 million pounds of oil were reported operating in Turkey and it was stated that approximately two-thirds of Turkey's annual cottonseed output was consumed for oil manufacture, with the oil being utilized both for edible purposes

and in soap manufacture. The cottonseed cake produced was said to be used locally for fuel, with small quantities being exported.

Cottonseed has never been an important item in Turkish foreign trade. Exports in 1941, the highest year during the 1937–42 period, comprised only 5,500 tons, and average shipments, 1940–42, comprised less than 4,000 tons annually. These quantities moved principally to the United Kingdom, Malta, and Germany. Turkish foreign trade data show no shipments of cottonseed oil.

There is some indication that Turkey's cotton output and consequent cottonseed production may increase in the postwar period. Acala cotton, an American type introduced into Turkey in 1940–41, has proved very successful, and producers are gradually replacing American Cleveland and a native cotton called Yerli with the Acala. There are also plans to begin extensive irrigation projects in the Cilician Plain area, which provides 66% of Turkey's total cotton crop. It is stated that yields will show an increase of from 200 to 250% as a result of irrigation in this district. If these plans are carried out, the Turkish cotton crop can be expected to reach approximately 600,000 bales of cotton in the postwar period, compared with a 1936–38 average of 280,000 bales. If seed were recovered on a commercial basis from this entire crop, cottonseed output in the postwar period would comprise more than 340,000 tons, compared with the 1937–39 average of less than 160,000 tons.

B. Uganda

Uganda is the second most important cotton-growing area in the British Empire, ranking after India. The cotton industry dates back to 1904–05, when 54 bales, valued at £236 were exported. Cultivation has shown a steady upward trend with acreage rising from 50,000 acres in 1912–13, to 345,000 in 1922–23, and to 1,071,000 acres in 1932–33. The area in cultivation during the most recent prewar years 1935–36 to 1938–39 averaged 1.5 million acres. Figures are not available for the years 1939–40 and 1940–41, but there was a decline during the war years. Acreage was reported at 875,000 acres for 1942–43 and 1.1 million acres for 1944–45.

Cotton production is carried on in all districts of Uganda except Kigezi and Karamoja, but two-thirds of the crop originates in Buganda Province, and the Busoga, Budama, and central districts of the eastern province. Planting occurs in the May–September period (depending upon the district) on plots ranging from "the size of a tablecloth" to small farms of 5 to 10 acres. Harvesting begins in November and continues through April.

Uganda's entire crop is ginned domestically, and in 1938, 143 gins were operating, with 151 additional plants idle. Gins are largely owned by Indians, although in 1938, seven European firms held interests in Uganda

gins. Farmers sell directly to the ginners, and there is very little middleman activity.

Domestic demand for cottonseed in Uganda is limited, and practically the entire production is exported. The size of these shipments varies, depending upon foreign cottonseed prices. As transportation costs are high, recovery of seed is not profitable when prices are below normal. Production of cottonseed for 1944–45, which reflects the wartime loss of foreign markets, is placed at 9,300 tons. The average output for the years 1934–35 to 1938–39 amounted to more than 160,000 tons. There is no commercial production of cottonseed oil in Uganda, and domestic use of seed is confined to the small quantities utilized for fuel by the gins and still smaller amounts used for fertilizer by the coffee estates.

During 1938 and 1939 experiments were carried on to determine the possibility of utilizing cottonseed oil as a Diesel fuel. No commercial extraction resulted, but an oil yield of 11% was reported.

Shipments of cottonseed from Uganda have been principally to the United Kingdom. Of the 1938 total of 137,000 short tons, 135,000 moved to Great Britain. In more recent years Australia and Japan have received the bulk of the small amounts not destined for the United Kingdom. Exports declined drastically as a result of the war, comprising less than 3,000 tons in 1941, 23,000 tons in 1942, and only 11 tons in 1943. In 1940 Uganda official trade statistics for the first time report shipments of cottonseed oil, and exports of oil are also shown in 1941 and 1942. As no cottonseed oil is known to be produced, it is likely that these amounts, which were very small, totaling 153 pounds in 1940, 1,000 pounds in 1941, and 10,000 pounds in 1942, represent a reexport item. Almost the entire quantity was shipped to Tanganyika, and no further exports are reported in 1943.

It is stated that Uganda's cotton acreage could be expanded to 2 million acre levels, approximately 37% above the 1934–35 to 1938–39 average of nearly 1.5 million acres. Abundant and suitable land is available in certain areas of Buganda Province and the eastern and western provinces. Unfortunately such an expansion would be retarded by the absence of roads and an adequate water supply and by the distance of these areas from railheads.

Presently there is no indication that cottonseed crushing on a commercial scale will be attempted in Uganda. Consequently any increase in actual seed production is dependent upon the state of foreign demand.

C. Anglo-Egyptian Sudan

Despite the organized and rigorous efforts of the Anglo-Egyptian Sudan Government, it does not appear likely that the Sudan will ever assume significance on world cotton markets. The extensive irrigation

projects which have been developed in the last twenty-five years have resulted in increased cotton acreage and production, but have not in any way lived up to early expectations.

Cottonseed output in the Sudan reached a peak of 133,000 tons in 1937–38. Production for 1942–43, the latest year available, comprised 100,000 tons.

Apparently cotton is indigenous to the Sudan, but development programs were not instituted on a wide scale prior to World War I. At that time English spinners were seeking additional cotton supplies from British Empire sources, and consequently every effort was made to increase output in the Anglo-Egyptian Sudan. Extensive irrigation projects were undertaken, but the resultant increase in production has never constituted as much as 10% of the anticipated Sudan potential. There are six cotton-growing regions in the Sudan: the Gezira section, completely under government control and producing the most important share of Anglo-Egyptian Sudan's cotton output; the Nile valley area, where private plantations operate; Tokar and Kassala, largely under government control; and the Nuba Mountains and Southern Provinces where the Government also exercises strong control.

Two British firms, the Sudan Plantation Syndicate and the Kassala Cotton Company, operate the Gezira section on concession. Here the government supplies the water, native labor is utilized, and the British firms provide all necessary supervision. Net proceeds are divided three ways: 40% to the government, 40% to labor, and 20% to the companies. The entire production process here is highly systematized. Planting is carried on during the month of August; harvesting begins in December or January and is completed by April or May. Each native grower is assigned 30 acres of land, but not more than one-fourth or one-third is planted with cotton in a given year. Two gins operated by the Syndicate handle the entire Gezira crop. To a large degree the quantity flow system of irrigation makes cultivation in this area possible. Water is supplied by the Sennar Dam on the Blue Nile (completed in 1924–25).

The Nile valley area is irrigated by a system of licensing pumps, operated by the government. In addition to government cotton cultivation, there are private cotton holdings, ranging in size from a few acres to more than 5,000 acres. Plantings and harvesting seasons are similar to those of the Gezira section.

Flood irrigation supplies the necessary water for Tokar and Kassala. The Braka Amer floods occur in the July–September period, and no additional water is supplied the cotton crop. The government supervises all phases of cotton growing and marketing in these two areas. Native growers are alloted a definite number of acres for cotton culture and additional land for food crops. Tokar cotton is ginned either at a private

plant at Suakin or at a government establishment at Port Sudan, where all Kassala cotton is ginned.

The quantity of rain-crop cotton grown in the Sudan is not large. Production without irrigation is carried on in the region of the Nuba Mountains and the southern provinces. Nuba Mountain cotton is ginned at Kadugli and Talodi, and that of the southern provinces—at Torit Maridi and Yei.

Domestic consumption of cottonseed is limited, although the exact quantity used domestically is not known. There is one small cottonseed oil mill at Kadugli, which in 1940 was the only vegetable oil press in the Sudan. Output of this plant amounted to 430,000 pounds in 1937–38 and was consumed entirely in the province of Kordafan by the local soap-making industry.

During the period 1937–39 cottonseed exports averaged 109,000 tons, compared with a reported production of 142,000 tons. Practically all pre-war cottonseed shipments moved to the United Kingdom, with only very minor quantities being destined for Denmark and Arabia. Anglo-Egyptian Sudan trade statistics are not available for the war years, but it is known that the bulk of the cottonseed leaving the area was shipped to Egypt where the derived oil was largely consumed by the British and Allied armed forces.

The past history of cotton culture in the Sudan does not indicate that cotton production there will expand markedly in the postwar period. Any sizable increases are definitely limited by the amount of tillable land, the problems of irrigation, and the limited supply of dependable labor.

D. Peru

Cotton, the basis of one of Peru's most important industries, is an indigenous crop. Although cotton was produced through the colonial period and in the early years of independence, no real development of the industry occurred until the early twentieth century. Beginning with 1908 the output of cotton rose sharply Exports of lint cotton increased from approximately 9,000 tons, 1900–07 average, to nearly 18,000 tons in 1908. The outbreak of World War I gave added impetus to the cotton industry. The rising production of cottonseed after that time indicates the rapid rate of growth.

In 1915–16 cottonseed output was placed at 52,000 tons; by 1920–21 this figure had reached 93,000 tons; and in 1935 a peak of 161,000 tons was reported. Production of cottonseed decreased somewhat after that date because of the loss of foreign markets for Peru's cotton. Despite the high domestic demand for cottonseed oil during the war period, seed output showed a declining trend and in 1943–44 totaled only 96,000 tons, the lowest figure since 1928.

Cotton cultivation is carried on principally in the irrigated valleys of the Pacific Coast region; less significant quantities are grown in a few inland districts. A considerable amount of capital is required for most efficient production in Peru, and the bulk of the crop is harvested from large plantations. Sowing seasons vary, according to the particular regions, but the most common planting period is in the months of September–November. However, in some instances, planting occurs as early as June, and in the Pervia section, sowing does not begin until January. Two planting seasons are followed in the Chincha and Ica valleys: December–February and May–June.

Of the 89 Peruvian cotton gins operating in 1938 the major share was in the hands of plantation owners. However, these gins also do some outside work for small growers, who usually pay the ginning fee in cottonseed, although in some instances the seed cotton is sold before ginning. Gins of United States manufacture are most common, and saw gins are more in demand than those of roller type.

Domestic cottonseed crushing has increased markedly during the last two decades. In 1928 cottonseed oil production was placed at 21 million pounds, of which 70% (nearly 15 million pounds) was exported. During 1944–45 (when cottonseed processed totaled 112,000 tons) 39 million pounds of crude oil, 59,000 tons of cottonseed cake, and 34,000 tons of husks, linters, impurities and waste were produced. Further processing resulted in the production of 10 million pounds of vegetable shortening, 10 million pounds of refined oil, 5.7 million pounds of deodorized oil, and 2 million pounds of winterized oil, with 724,000 pounds of oil being consumed in the crude form. In the 1944–45 season 20 mills were operating, including 10 in the Lima district, 5 in Ica, 3 in Piura, and 2 in Arequipa.

The war brought about an increase in domestic demand for cottonseed oil, to replace former imports of coconut oil, olive oil, and lard. Curtailment of Peru's cotton crop, however, prevented any marked rise in crushing operations, and cottonseed oil production, which totaled 37 million pounds in 1938, reached a wartime peak of only 45 million pounds in 1943. Exports of cottonseed oil from Peru have never been significant, comprising 120,000 pounds in 1937, a record of 718,000 pounds in 1939, and 472,000 pounds in 1941, the last year in which cottonseed oil shipments were reported. Despite strong demand it does not appear that there has been any great increase in actual domestic oil consumption during the war years.

Exports of cottonseed declined sharply during the course of the war. Cottonseed shipments, which amounted to 47,000 tons in 1937, fell to 30,000 tons in 1940, and 6,000 tons in 1942. On January 31, 1943, all further exports of cottonseed were banned by the Peruvian Government. The bulk of Peru's former cottonseed exports moved to Chile.

A serious problem was created by the wartime loss of foreign markets

for cottonseed cake, which had moved principally to Denmark and Germany, and to a lesser extent to the United Kingdom. Domestic consumption of this commodity was small in prewar years, and large surpluses were accumulated as a result of the decline in exports. Cottonseed cake shipments decreased from more than 46,000 tons in 1939 to less than 3,000 in 1941.

Increased production and exporting of cottonseed meal compensated to some degree for the lost cake markets. Exports of meal increased from 6 tons in 1939 to 26,000 tons in 1941, with 1940 and 1941 shipments moving principally to the United States. In addition to the quantities exported, approximately 8,000 to 14,000 tons of meal mixed with guano is used locally as a fertilizer.

As Peruvian cotton growing is definitely limited by the area of suitable land, there is little likelihood that Peru will ever become one of the world's major producing areas. At the same time, Peru's long-staple cotton commands a premium on world markets, and there is every indication that acreage will continue to expand, although probably not at the prewar rate. As cottonseed oil products are now firmly established on the Peruvian market, it may be expected that domestic consumption of cottonseed will rise, and output of cottonseed oil will expand in the postwar period.

E. Mexico

Cotton is thought to be indigenous to Mexico, and it grows wild in many parts of the country. Cultivation of cotton, carried on to some extent during the colonial period, increased considerably after Mexican independence was established. However, until World War II, shipments to foreign markets were not significant, comprising no more than 10% of the total cotton crop.

As a result of the greatly expanded market for Mexican textiles in the other Central American republics, output of cottonseed increased sharply during the war years. Seed production totaled 209,000 tons in 1943, and is estimated at 215,000 tons for 1944, with the 1945 cotton crop expected to yield 184,000 tons of seed. These figures compare with 1937–39 average output of 137,000 tons.

Mexican cotton cultivation is carried on most extensively in northern Mexico. The Laguna District is the most important cotton area, followed by the Districts of Matamoros, Mexicali, Delícias, and other regions in the State of Chihuahua, the Juarez valley area, Don Martín, and the Pacific Coast regions: Sinaloa, Sonora, and Nayarit. The bulk of the crop is grown on irrigated land, and planting usually begins in the month of February, but sowing is sometimes postponed as late as June. Cotton picking generally starts in July, and occasionally is not completed until November.

Some of the large plantations own and operate their own gins. In former times cotton cultivation on large holdings was the general rule, but since the recent breaking up of large plantations, cotton is being grown more on small land holdings. This has caused some temporary disorganization of the cotton industry, because of the small farmers' unfamiliarity with marketing methods. Many of these small cotton growers have been financed by private corporations engaged in ginning operations or the buying of cotton or cottonseed. The usual method of marketing cotton in Mexico is direct from grower to ginner, with most gins being located in growing areas.

Nearly all the Mexican cottonseed crop is crushed by domestic mills. Cottonseed comprises Mexico's second most important source of vegetable oil. Since 1943 sesame seed has been the primary source, and in the prewar period, copra, largely imported, represented the most important oil-bearing raw material. Oil production was reported to total 63 million pounds in 1943, with the 1944 and 1945 outputs tentatively placed at 66 and 55 millions pounds, respectively. This level is approximately 60% above the average 1937–39 production.

Cottonseed oil is sold on the Mexican market for edible purposes, and also, particularly since the war, is consumed in considerable quantities as an industrial oil. Loss of former copra imports has resulted in a very tight soap material situation, and cottonseed oil has substituted for coconut oil in the soap kettle.

Mexico's foreign trade in both cottonseed and cottonseed oil has always been limited. Yearly seed imports ranging between 1,000 and 2,000 tons are ordinarily utilized for planting purposes. This seed originates in the United States and is used to prevent any deterioration in Mexican cotton crops; approximately one-fourth of Mexico's annual cotton acreage is planted with imported seed. Cottonseed exports are irregular and insignificant in amount. During the period 1934–43, shipments to foreign markets were reported in only three years, 1940, 1943, and 1944, with 1943 exports, the highest on record, totaling less than 180 tons. Exports of cottonseed oil are also very small and have been sent principally to the United States. Approximately 2.5 million pounds were shipped in 1941, all to the United States, with 2 million pounds exported in 1942. These are the only considerable amounts to leave the country since 1930, except during the three-year period 1934–36, when annual cottonseed oil exports averaged 5 million pounds.

Continuance of Mexican cotton acreage at wartime levels or further expansion depends upon the maintenance of foreign markets for Mexican cotton and cotton textiles. Acreage could be increased in the Laguna District and in the Don Martín project, particularly if additional irrigation facilities were provided.

When copra imports are again available there is some question as to whether cottonseed oil consumption will continue at the wartime rate. However, it is unlikely that either cottonseed or cottonseed oil production in the next several years will be sufficient to result in any burdensome surplus.

F. Argentina

Argentina production of cottonseed from the 1944 crop totaled 241,000 tons, the highest figure yet recorded for that country. Output at this level compares with the average 1939–43 production of less than 150,000 tons. A severe drought in the growing season resulted in a 1945 output of but 187,000 tons, a considerable reduction from that of the preceding year.

Cotton cultivation, carried on intermittently in Argentina since 1500, began a period of increase in 1911 and has expanded rapidly since 1923–24. The area planted in 1944 totaled 944,000 acres, compared with 155,000 acres in 1923. Much the greater part of this increase occurred in the Chaco, Argentina's principal cotton-growing region, where government-encouraged colonization has met with some success. Other major cotton growing areas, located principally in the northern part of the country, as is the Chaco, include the provinces of Corriente, Santiago del Estero, Santa Fe, and the Territory of Formoso. Cultivation methods are patterned largely after those of the United States, and many American varieties are grown. Argentine cotton farms are small, with average planted areas in the growing regions varying from 2 to 44 acres. These farms growing cotton numbered 25,283, according to the 1935–36 census, and a major percentage comprised enterprises operated by "squatters." Of the total number of cotton-raising establishments, 13,390 were in the hands of "squatters," 7,594 were operated by renters, and only 4,241 were operated by landowners. Argentine seasons are approximately the reverse of those in this country, and the Argentine cotton harvest begins in April and reaches a peak in May, continuing until October. Ginning is carried on in the growing areas. Of the total of 118 gins operating in Argentina in 1937, 78 located in the Chaco ginned 66% of the total crop.

Cottonseed oil, which prior to 1937 was the principal edible oil produced in Argentina, has declined in relative importance on the domestic market during recent years. This is largely the result of the greatly increased output of sunflowerseed oil, which has replaced Argentina's former olive oil imports. Cottonseed oil production has also increased, but not as sharply as has sunflowerseed oil. Of the total 630 million pounds of vegetable oil processed in Argentina in 1942, cottonseed oil amounting to 40 million pounds comprised only 6%. Cottonseed oil exports have increased greatly in recent years. Shipments, negligible in the 1937–40 period, increased to 16 million pounds in 1941, and in 1942 reached a peak

of 44 million pounds in 1943. They totaled 32 million pounds in 1944. Foreign markets for the oil have been principally Switzerland, Sweden, Canada, and the United States. Cottonseed exports from Argentina have never been sizable, but cottonseed cake has been shipped in considerable quantities. During the period 1937–39 an average of 49,000 tons left the country destined mainly for Denmark, Sweden, the United Kingdom, and Germany. The 1943 total amounted to 29,000 tons, which went almost entirely to Sweden. Because of fuel shortages, Argentina burned considerable quantities of cottonseed cake in the war years.

With the cultivation of cotton concentrated in the Chaco area, expansion of the crop depends almost entirely upon the movement of colonists to that region. A cotton-growing potential of 50 million acres is reported for all of Argentina, compared with the 1944 harvested area of approximately 800,000 acres. Favorable factors encouraging the development of the Argentine cotton crop are high soil fertility and corresponding good yields, absence of plant diseases and pests, cheap land, and low production costs. Limiting factors are insufficient transportation, a scarcity of labor, and limited technical knowledge of the crop.

G. Iran

Iran is one of the oldest of the cotton-growing countries, but Iranian production has never gained major importance in world markets. Khuzistan is the most important growing area, with potential cotton output there said to be equal to the combined production of all the rest of the country. Other sections producing a significant share of the total crop are Khorassan, Mazanderan, Gurgan, Isfahan, Shiraz, Kashan, and Tehran.

Cottonseed production reached a peak of 110,000 tons in 1938–39, and declined steadily from that time through 1944–45, the last year for which statistics are available. Seed output from the 1944–45 cotton harvest totaled only 13,000 tons, a decline of 88% from the 1938–39 record. This very sizable decrease in Iranian cottonseed production reflects the loss of foreign markets for both cotton and cottonseed, the low price for cotton in comparison with other agricultural products, and the shift of labor supply from rural districts to centers of war activity.

Cotton cultivation in Iran is carried on by the most primitive methods. Land tenure is of a feudal nature, and peasants realize only approximately one-twentieth of the crop value after various charges by the landowners are met. As indicative of general production methods, fields are plowed by a crooked stick drawn by oxen. Plantings vary by regions, generally occurring in the months of February–April, and are completed for all areas by mid-May. The cotton harvest is accomplished by three annual pickings, as Iranian cotton matures first at the top and outside of the

plant, ripening more slowly at the bottom and inside. The harvest period continues from July through November.

As a general practice growers sell their raw cotton to speculators and private gins. The Iranian Government has attempted to check this custom—which results in the grower receiving relatively low prices—by operating gins and charging less to process cotton owned by the growers than for that in the hands of middlemen. In 1945 there were 77 gins in Iran: 27 government-owned, 43 operated by private business, and 7 owned by cotton growers.

The bulk of Iran's cottonseed output is utilized domestically, either for oil crushing, as a cattle feed or for planting purposes. Total home use amounted to 88 million pounds in 1942–43, 53 million pounds in 1943–44, and 49 million pounds in 1944–45. The largest share, 45% for the three years, was consumed as fodder, with the quantity crushed for oil varying from 18 million pounds in 1942–43, to 67 million pounds in 1943–44, and 12 million pounds in 1944–45. Reported oil production totaled 1.4 million pounds in 1942–43, 529,000 pounds in 1943–44, and 992,000 pounds in 1944–45. Oil yields at this level would be extremely low, comprising only 8% in each year, contrasted with an average of 15% for the United States. The bulk of the oil produced in Iran is consumed within the country.

Iran's foreign trade in cottonseed and cottonseed oil has never been significant. Seed shipments amounted to 1,000 tons in 1938, reached a peak of 10,000 tons in 1940, and declined sharply thereafter. No seed exports were reported for 1943–44 or 1944–45, and 1942–43 shipments totaled but 5 tons. During the period 1937–38 to 1939–40 the United Kingdom was Iran's best foreign market, and in 1940–41 and 1941–42 Japan received the bulk of all shipments. Exports of cottonseed oil were not reported separately until 1941–42, when they amounted to 2 million pounds, which moved almost entirely to the U.S.S.R. Cottonseed oil shipments declined to 111,000 pounds in 1942–43; all of this was destined for the Soviet Union. No exports were reported for either 1943–44 or 1944–45.

Expansion of cotton acreage in Iran is limited by the dry climate, which makes necessary extensive irrigation, by the outmoded methods of cultivation and land tenure, and by the fact that Iranian cotton is generally regarded as inferior. The Government has made several attempts to encourage cotton production in Iran, but none of their programs has proved markedly successful. However, there is every likelihood that output of both cotton and cottonseed will increase over wartime levels, as soon as Iran is able to ship to former European markets.

H. Chosen

Native cotton has been grown in Chosen from earliest times, but very little information regarding the industry there is available.

American type cotton was first introduced into Chosen in 1906. Early experiments carried on in the Province of Moppo with American cotton proved successful, and cultivation of this type has been encouraged since that time. Cotton is grown throughout Chosen, with the exception of the province of South Kankyo. Latest available data show the provinces of South Zenra, and North and South Keisho to be leading in production.

In line with the Japanese policy of increasing output of all essential raw materials, a ten-year plan for expanding Chosen's cotton output was instituted in 1933. A cotton production goal of 420 million kin of raw cotton (approximately 385,000 bales ginned) was announced, and projected plantings were placed at 350,000 chobu (860,000 acres). These figures compared with an actual 1932–33 output of 130,000 bales of ginned cotton on 390,000 acres. This program was fairly successful, and cottonseed output rose from an average of 65,000 tons from 1930–31 to 1934–35, to 94,000 tons for the five-year period 1935–36 to 1939–40, and reached 108,000 tons in the 1940–41 season. A comparable gain is shown in the output of ginned cotton, with production rising from 128,000 bales in 1932–33 to a record of 204,000 bales in 1937–38, with the latest available statistics showing a crop of 186,000 bales in 1940–41.

No production data are available for Chosen's production of cottonseed oil or oilcake. However, cottonseed oil was reported to be produced by at least one factory, and the 1936 output was valued at 1,320 yen, of a total vegetable oil production worth 5,782,000 yen (383,000 and 1,678,000 dollars, respectively).

Chosen's foreign trade in cottonseed and cottonseed oil has been confined almost exclusively to Japan. Shipments of cottonseed to Japan amounted to 4,705 tons in 1936, with exports to other areas comprising 186 tons. Average annual exports of seed to Japan, 1937–39, amounted to 12,000 tons, while at the same time quantities destined for other countries averaged only 455 tons. Japan's receipts of Chosen cottonseed comprised 19,000 tons in 1940, but exports to other destinations are not shown in that year. Cottonseed oil shipments to countries other than Japan are not shown separately in Chosen foreign trade statistics. Exports to Japan for 1936–40 averaged 6.4 million pounds yearly.

As Chosen's foreign market is so definitely associated with Japan, continued development of the cottonseed industry is likely to be dependent upon Japan's ability to make purchases in the postwar period. Domestic demand for cottonseed (derived by subtracting cottonseed exports and the seed equivalent of oil shipments) averaged only approximately 12,000 tons a year in the prewar period. Home consumption at this rate accounted for only 25% of production during 1936–40. It is most unlikely that domestic utilization will expand sufficiently to absorb Chosen's entire output.

IX. Major Cottonseed Consumers among Nonproducing Countries

Much the greater part of all cottonseed produced is consumed within the country of origin. Nevertheless, shipments have been sufficient to result in a sizable cottonseed crush in certain noncottonseed producing countries. Chief among these is the United Kingdom, with Japan and Chile next in importance, and several continental nations consuming less significant amounts of imported cottonseed.

A. The United Kingdom

World exports of cottonseed averaged 661,000 tons during the period 1930–34. Of this total, 584,000 tons or 83% was destined for the United Kingdom. Foreign trade statistics for the United Kingdom report even heavier receipts for 1937–39, when average annual imports comprised 679,000 tons. Thus Great Britain had at her disposal a supply of cottonseed larger than that of any other nation, excepting only the six major producing countries: the United States, India, the Soviet Union, China, Brazil, and Egypt.

Approximately one-half of the total receipts was shipped from Egypt, and the bulk of the remainder was supplied by the Anglo-Egyptian Sudan and Brazil. Great Britain also imports minor quantities of cottonseed oil—an annual average of 8.8 million pounds of crude oil and less than 1 million pounds of refined oil in 1937–39. Crude shipments were mainly from Egypt, with Brazil and Burma the major source of refined oil.

All the cottonseed imported into the United Kingdom is absorbed by the domestic crushing industry. A considerable, although not the major, share of the resultant cottonseed oil is exported. Average shipments of crude oil amounted to 18 million pounds and of refined oil, 13 million pounds, for the period 1937–39. Canada and the United States have been Great Britain's best customers for this oil, together receiving 78% of all crude oil and 92% of all refined oil leaving the country during the years 1937–39. British colonies and continental European countries absorbed the bulk of the remainder.

Considerable quantities of cottonseed oil are also consumed on the British market, although cottonseed oil is not nearly as important a source of vegetable oil in the United Kingdom as it is in the United States. Total British vegetable oil supplies averaged 1.2 billion pounds for the period 1933–37, of which cottonseed oil to the amount of 190 million pounds represented less than 15%. During these years the shortening, margarine, and soap industries of the United Kingdom reported an average annual use of 55 million pounds, 28 million pounds, and 4 million pounds of cottonseed oil, respectively. In 1937 cottonseed oil comprised 37% of all

fats and oils utilized in shortening, 9% of the total consumed in margarine, and less than 1% of the fats and oils used in the soap kettle.

B. Japan

Cottonseed receipts of Japan, which ranks second among importing nations, are very small in comparison with the amounts entering the United Kingdom.

Japanese incoming shipments of cottonseed totaled 118,000 tons in 1937 and 71,000 tons in 1938, the last year for which full trade figures are available. The bulk of this supply originated in China, with Manchukuo the next most important source, and minor quantities coming from Iraq. Japanese statistics also report minor receipts of cottonseed oil: 14 million pounds in 1937 (13 million from China and 1 million from the United States) and 185,000 pounds in 1938—all from the United States.

The bulk of Japan's cottonseed oil supplies, comprising the oil equivalent of imported seed (converted at 15%) plus cottonseed oil receipts, amounted to 49 million pounds in 1937 and 21 million pounds in 1938. Exports of cottonseed oil from Japan in those years totaled 45 million pounds and 12 million pounds, respectively, shipped principally to the United States.

Statistics relative to Japanese consumption are not available, but it is likely that the bulk of the remainder, 5 million pounds in 1937 and 9 million pounds in 1938, was utilized by the domestic fish canning, margarine, and soap industries. As the commodities manufactured by these trades were also sold on world markets, actual Japanese consumption of cottonseed oil was probably considerably below the 1937–39 average of 7 million pounds, which was available after providing for exports in the form of oil.

C. Chile

In contrast to Japan, where the bulk of the oil derived from cottonseed imports is exported, Chile utilizes all cottonseed receipts domestically. Seed imports into Chile, third most important importing nation, averaged 49 thousand tons for the period 1937–39, declining to 40 thousand in 1940, 9 thousand in 1941, and 6 thousand tons in 1942. Wartime conditions account for the decrease in the later years. During the years 1937–39 Peru was Chile's most important source of cottonseed, followed by Egypt. Increased domestic consumption in Peru and Egypt and wartime shipping conditions later caused a sharp decline in Chilean imports of Peruvian seed and eliminated Egypt as a source of supply. Although Brazil exported 11 thousand tons of cottonseed to Chile in 1940, no other country has shipped in quantity to Chile in that year. During both 1941

and 1942 Peru still supplied most of the Chilean receipts, although in greatly decreased amounts.

Chile also imports some cottonseed oil. Incoming shipments amounted to 6,000 pounds in 1937, increased to 190,000 pounds in 1940, and were over 1 million pounds in 1942. Receipts declined to 401,000 pounds in 1942. In the prewar period Italy and France were the main sources, and beginning with 1940, Brazil has been the principal supplier.

Domestic production of oil-bearing materials, although increasing in recent years, supplies only a minor share of Chilean vegetable oil needs. During recent years 80 to 90% of the vegetable oil consumed in Chile has been produced from imported oil-bearing seeds and nuts.

The prewar oil capacity of the seven principal oil mills in Chile was placed at 37 million pounds, with the 1937–39 output approximately one-half that figure. Cottonseed oil comprised 90% of the total oil produced.

Since the war, vegetable oil production in Chile has increased considerably, and the output of sunflowerseed oil, which has largely replaced cottonseed oil on the Chilean market, amounted to 28 million pounds in 1943 and 53 million pounds in 1944.

As a by-product of the crushing industry, Chile in the prewar period had a considerable surplus of cottonseed cake. In 1939 exports of this commodity totaled 16,000 tons, of which more than 95% moved to Denmark and Sweden. Since the wartime cut in cottonseed imports, cottonseed cake exports have virtually disappeared, and it is reported that the entire Chilean output is consumed as a cattle fodder by the local dairy industry.

D. Other Cottonseed Consumers

World imports of cottonseed averaged 900,000 tons for the period 1936–38. Of this total the combined receipts of the United Kingdom, Japan, and Chile comprised 94%. The only other countries importing sizable amounts of cottonseed in the prewar period were Denmark, Germany, Greece, and Malta. When average incoming shipments for these countries are considered, in addition to those of the three major importing nations, 97% of world cottonseed receipts are covered.

Denmark's imports of cottonseed totaled 6,000 tons in 1937, 13,000 tons in 1938, and 9,000 tons in 1939. The United Kingdom was the sole source of supply in all three years, but these quantities represented transshipments, probably from Egypt. In addition to cottonseed, Denmark also imported 2,000 pounds of cottonseed oil in both 1938 and 1939. The United Kingdom supplied all 1939 receipts and the 1938 total was received from "Southwest Asia."

All seed receipts were crushed by Denmark's domestic oil industry, which operates on a modern and extensive basis. Cottonseed is one of

the minor raw materials utilized by Danish oil mills, with cacao beans, palm kernels, peanuts, sesame seed, and soybeans taking precedence over cottonseed.

During the prewar period total Danish cottonseed oil supplies amounted to approximately 2.8 million pounds annually. Of this total, oil exports averaged 595,000 pounds, principally to Sweden and Switzerland. The remainder was utilized domestically in the margarine industry, and to a lesser extent consumed directly as a salad or cooking oil.

German imports of cottonseed averaged less than 7,000 tons for the period 1936–39, of which Peru, Brazil, Nicaragua, and Egypt were the principal suppliers. Average cottonseed oil imports during the same years comprised 6 million pounds. Both the cottonseed oil imported and the oil obtained from cottonseed were utilized almost entirely on the domestic market. German trade statistics report no exports of cottonseed, and shipments of cottonseed oil are recorded in only one year 1937, when they amounted to but 664,000 pounds, destined mainly for Czechoslovakia.

Cottonseed oil was not a major oil on the prewar German market, where whale, soybean, peanut, palm kernel, and coconut oils were of considerably greater importance. Statistics relative to the consumption of cottonseed oil in Germany are not available, but it is probable that the bulk was consumed in the local margarine industry.

Cottonseed imports into Greece amounted to only 205 tons in 1937, 9 tons in 1938, and 10 tons in 1939. The United States supplied the 1937 and 1938 shipments, and Egypt was the source in 1939. In addition, Greek trade statistics report 1937 cottonseed oil receipts of 2 million pounds, principally from Egypt. No further oil imports are shown. As Greece exports neither cottonseed nor cottonseed oil, it is assumed that incoming shipments of both seed and oil were consumed domestically.

Imports of cottonseed into Malta amounted to 5,000 tons in both 1937 and 1938, the latest years for which trade data are available. Turkey and Syria were the sources of supply. No exports of either cottonseed or cottonseed oil are reported, and oil imports are included with all other vegetable oils.

It is unlikely that cottonseed exports will again reach prewar levels. Most countries which previously shipped the seed are now crushing greater quantities for home consumption and any exports will probably be in the form of oil.

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B. COMPOSITION AND CHARACTERISTICS

CHAPTER III

STRUCTURE OF THE COTTONSEED

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I. Introduction

Commercial cottonseed, used as an oleaginous raw material or as seed for planting purposes, have been "ginned" of their staple fiber. The North American upland type of cottonseed, *Gossypium hirsutum,* even after ginning, is densely covered with short cotton fibers or "linters," and as a result the nondelinted seed appears to be white or gray in color. Beneath the linters, however, is the seed coat from which the linters

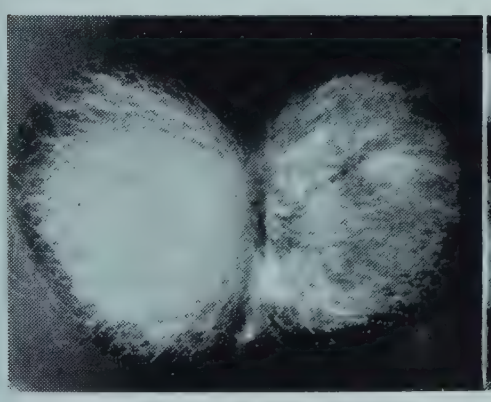


Fig. 1. Enlarged photograph of "seed cotton" with the fibers combed out along the raphe.

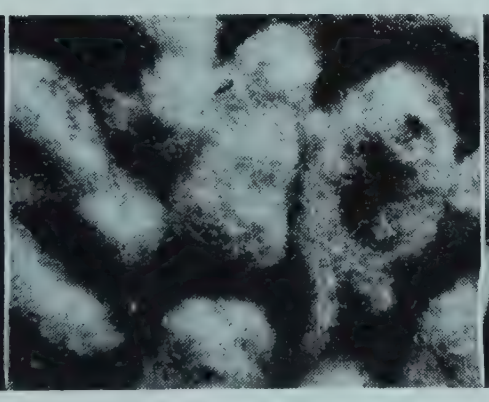


Fig. 2. Cottonseed after ginning are densely covered with short fibers, known as linters.



Fig. 3. Delinted cottonseed. See text for description.

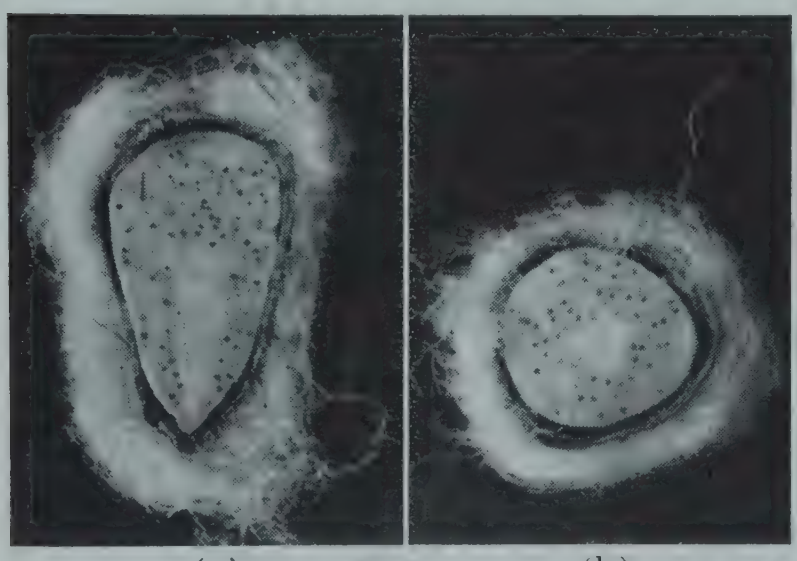
arise. The seed coat is more commonly black than any other color, however, it may vary from brownish-red to jet black. It is in the form of a pointed ovid, between 8 and 12 mm. in length. Egyptian or "Sea Island" cottonseed, *Gossypium barbadense,* have no adhering linters and are properly described as black in color. North American upland cottonseed weigh 32 pounds to the bushel.

Trade practices have made a physical division of "seed cotton" into staple cotton and cottonseed so common that we accept the differentiation in a manner which suggests that two distinct products are derived from the cotton plant. It is a fact, nevertheless, that staple cotton is as

much a product of the cottonseed as are oil, linters, meal, and hulls. The long fibers comprising staple cotton extend themselves from and are attached to the seed coat or hull in the same manner as the short fibers or linters. It is proper, therefore, to describe the cottonseed as a product of the cotton plant comprising two principle parts: the hull or spermoderm from which staple cotton and cotton linters arise, and the kernel or embryo from which oil and meal are obtained. Figure 1* is a photograph of "seed cotton" with the staple cotton combed out along the raphe. Figure 2 is a photograph of "seed cotton" after ginning, which removes the staple cotton leaving the "linty" cottonseed as a residue.

II. Gross Structural Characteristics

The cottonseed is anatropous, *i.e.*, characterized by an inverted ovule and micropyle bent down toward the funiculus. The ovule of the cottonseed is characterized by two integuments which develop into the hull or seed coat known as the spermoderm. In addition to the two principal elements of the seed, *i.e.*, spermoderm and embryo, there is a third structure, a membrane which completely envelops the embryo. This membrane may be described as a residual tissue of endosperm which supported the embryo development and perisperm, the remnants of the nucellus of the ovule. Moreover, an examination of delinted cottonseed, Figure 3, will disclose the presence of a single slight ridge, running longitudinally with the long axis of the seed, extending from the hilum to the chalazal. This ridge is known as the raphe; it is a characteristic of anatropous ovules. It contains the vascular bundles which supplied the developing seed with moisture and minerals.



(a) (b)

Fig. 4. Enlarged photographs of longitudinal (a) and transverse (b) sections through a cottonseed.

Cottonseed after removal of the lint are pointed ovoid, dark brown or nearly black, and vary up to 12 mm. in length. Both the hilum (point of attachment) and the micropyle (opening leading through the integument to the nucellus) are located at the pointed end, and the chalaza (point where the integument diverges from the nucellus) is at the other end, toward one side.

Figure 4 is a photograph of longitudinal and transverse sections of a cottonseed. The broader oval end of the seed is the chalazal end. The

* The author wishes to acknowledge with thanks the courtesy of Dr. Leta Henderson Webber and Dr. J. G. Woodroof for the preparation of the illustrations used in this chapter.

pointed tapering end of the seed is the micropylar end where the hilum and micropyle are located. The funiculus is at the extreme point of the micropylar end.

The cottonseed cross sections are of especial interest in respect to the embryo which discloses the cottonseed to be a dicotyledon, there being two large flat cotyledons and the so-called axial organs: the radicle, the hypocotyl, and the epicotyl. It will be noted that the cotyledons are folded around the radicle and over the top of the hypocotyl. On the embryo surface of the cross sections innumerable dark "specks" will be noted. The specks are pigment glands sometimes referred to as gum or resin



(a) (b)

Fig. 5. Enlarged photographs of partially unfolded (a) and completely unfolded (b) cotyledons.

glands, or cavities (see Chapter VI). They contain pigment materials which impart the characteristic yellow-red color to cottonseed meal and oil. Among the pigments is gossypol. The pigment glands are readily ruptured in the presence of water whereupon their contents flow out and discolor the cotyledon tissue. The gossypol, however, does not go into water solution but is oil-soluble.

In the tissue of the embryo are stored aleurone, oil, and starch grains, which serve as reserve nutritive materials for the germinating plant. Within the embryo, also, and originating within the radicle, are the vascular bundles, or circulatory system, which extend through the hypocotyl and spread out into the cotyledons.

Figure 5 is a photograph of partially unfolded and completely

unfolded cotyledons. The vascular system is distinctly outlined in the completely unfolded cotyledons. The cotyledons are observed to be kidney shaped.

III. Microscopic Structure

A. Cottonseed Hull

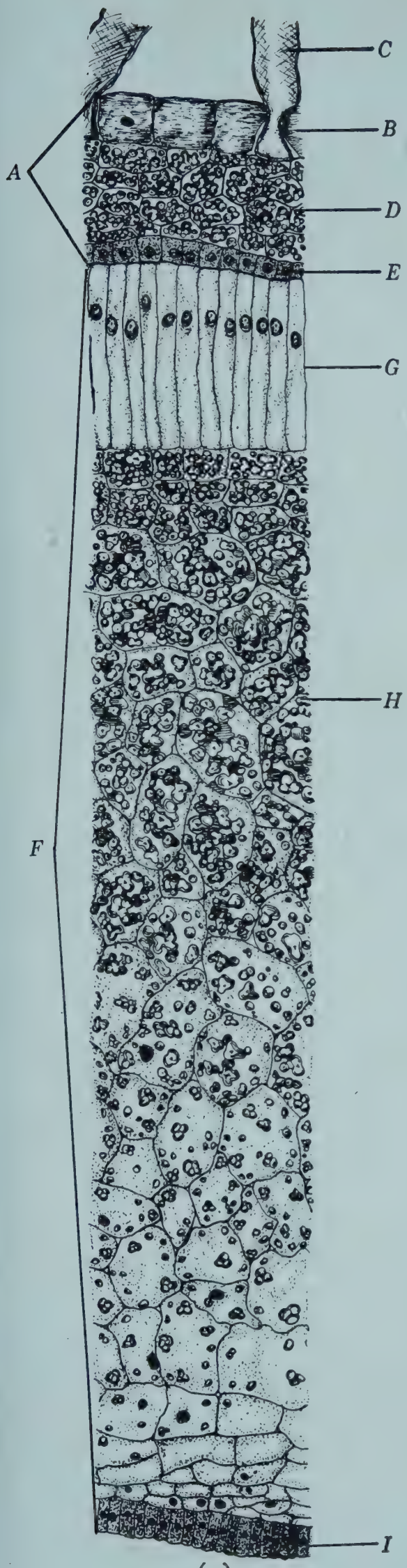
Figure 6a outlines the transverse structure of the mature or exhausted cottonseed hull (spermoderm) containing both staple cotton and cotton linters, both of which constitute cellular elements of the epiderm.

The spermoderm is characterized by two intimately associated integuments, one external and the other internal. Moreover, at maturity the thickness of the spermoderm has diminished by from one-half to two-thirds of its maximum (compare with Fig. 6b). The lateral shrinking of the spermoderm as maturity approaches occasions a collapsing of the cell structure, particularly with respect to the inner epidermal layer as well as the parenchyma cells of the inner integument. Associated with the collapse of these cells is the deposition of other materials forming the innermost structures referred to as "pigment layers." It is the practice, therefore, to refer to the innermost cell structure as "pigment layers." Figure 6b delineates the structure of the spermoderm before the seed is wholly mature when the cottonseed hull is storing nutrients for the developing embryo. Detail references are common to both figures.

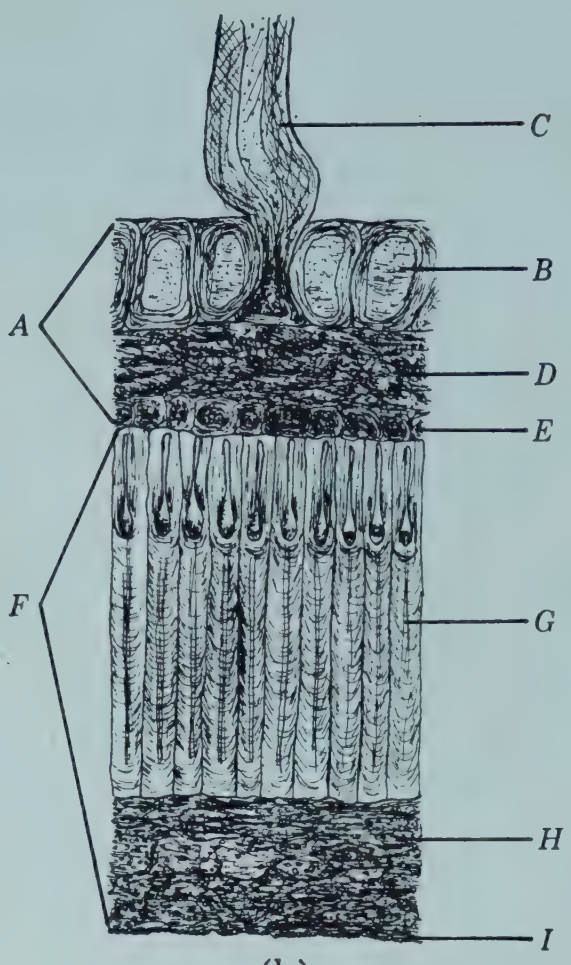
The external integment of the spermoderm is comprised of three distinct structures in addition to the fibers extruding from the surface of *B*, the outer epiderm, composed of cells of irregular shape but characterized by substantially thick cutinized walls enclosing tannin-containing compounds: *C*, fibers as single cells; *D*, parenchyma cells containing sugars and pentosans as principal constituents (at maturity this region is the outer pigment layer); *E*, the inner epiderm of empty, colorless, lignified cells, the arrangement of which are irregular in that at frequent intervals two small cells are superimposed and occupy approximately the same area as a single cell.

The internal integument of the spermoderm is also comprised of but three distinct cell structures: *G*, the outer epiderm being made up of a very unusual structure of palisade cells—the lower two-thirds of which are highly lignified, the upper one-third being characterized by a very narrow lumen ending in a pear shaped cavity; *H*, parenchyma cells, similar to *D*, but collapsed at maturity and generally classified as a pigment layer; *I*, the inner epiderm in the mature hull has lost its reserve of nutrients to the developing embryo—the cells are collapsed and constitute a second pigment layer.

Figure 7 is a diagrammatic outline of a longitudinal section of the spermoderm without reference to staple cotton or linters. In addition to



(a)



(b)

Fig. 6. Cross section through seed coat of mature (a) and twenty-day old (b) cottonseed: *A*, outer epiderm; *B*, epidermis; *C*, fiber; *D*, outer pigment layer; *E*, colorless layer; *F*, inner integument; *G*, palisade cells; *H*, inner pigment layer; *I*, inner epidermis.

the detail references commented on in respect to Figures 6a and 6b, the diagrammatic outline presents other elements of interest, *e.g.*, at *E″*, the chalazal cap, it will be noticed that the palisade cells, *D*, do not continue around the periphery of the spermoderm but terminate just short of meeting in the region of the cap. There is, however, an extraordinarily dense formation of parenchymatic tissue at the chalazal cap, the cell structure of which is oriented in a fan-like pattern. There are large intercellular spaces. When very dry, these cell layers appear to flake off or otherwise open up to make the area permeable. It is at the chalazal end of the seed that moisture first penetrates to the embryo, and at this point the membrane surrounding the embryo is attached to the seed coat, *G*,

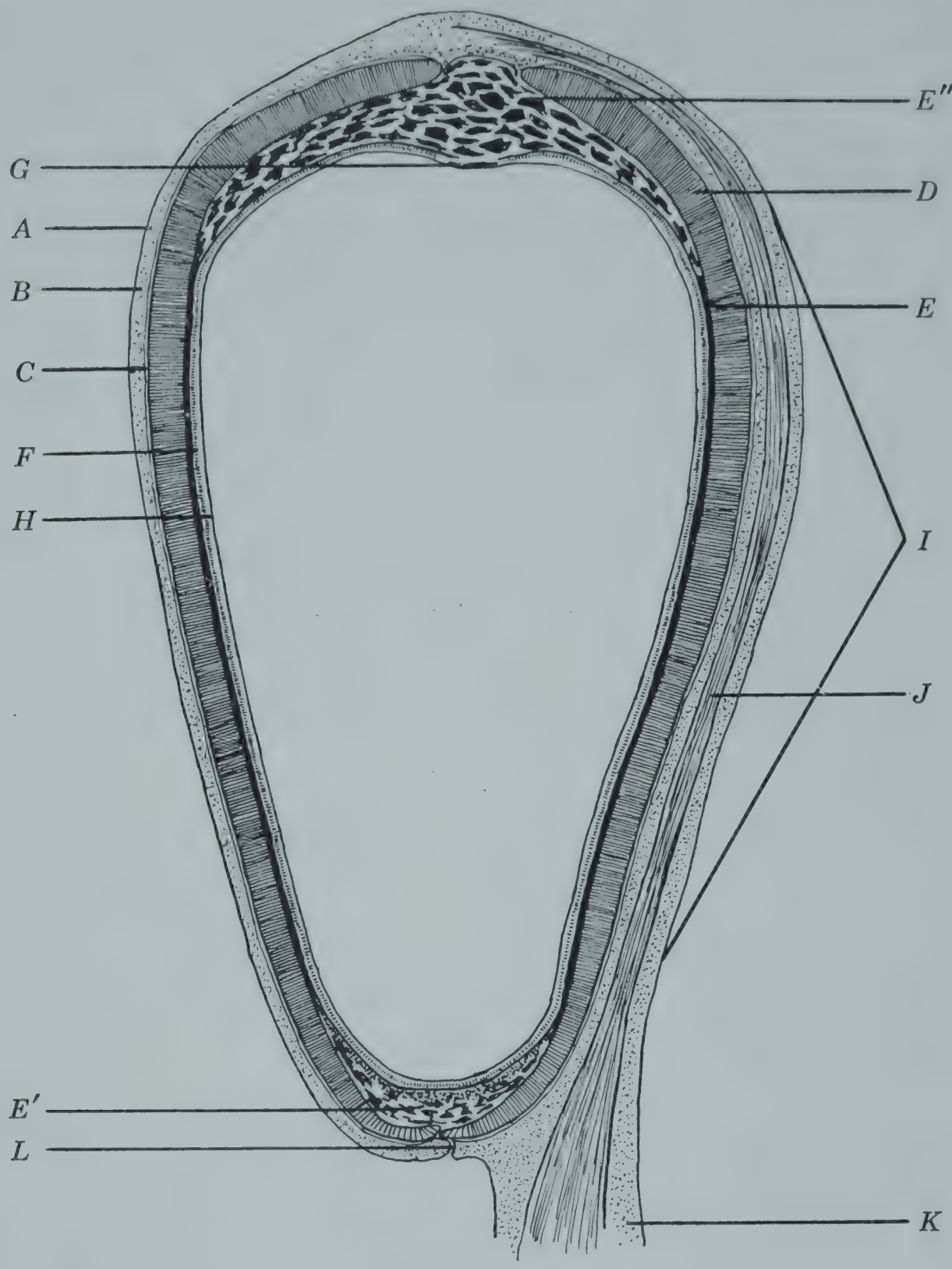


Fig. 7. Diagram of a longitudinal section through the layers of the cottonseed coat:

A, outer epidermis.
B, outer pigment layer.
C, colorless layer.
D, palisade layer.
E, inner pigment layer.
E′, inner pigment layer differentiated at micropylar end.
E″, inner pigment layer differentiated at the chalazal cap.
F, fringe cells.
G, specialized cells at base of chalazal cap.
H, membrane cells.
I, raphe.
J, vascular bundle.
K, funiculus.
L, micropyle.

and is the only point of attachment between the seed coat and the embryo. The micropyle is identified at *L*, where it will be noted that the palisade cells, *D*, as a continuous structure, distinctly terminate. The cells are so adjoined, however, as to completely enclose the micropyle. In the region

of the micropyle the palisade cells are disposed toward an inclined pattern and are not as fully or uniformly developed as in the side walls. During germination the root shoot extends itself downward through the micropyle. The funiculus, identified at *K*, is the short stalk which connected the seed to the mother plant at the placenta. Along one side of the seed, extending from the chalazal cap to the funiculus, is the raphe, *I*, which contains the vascular bundle, *J*, supplying the seed.

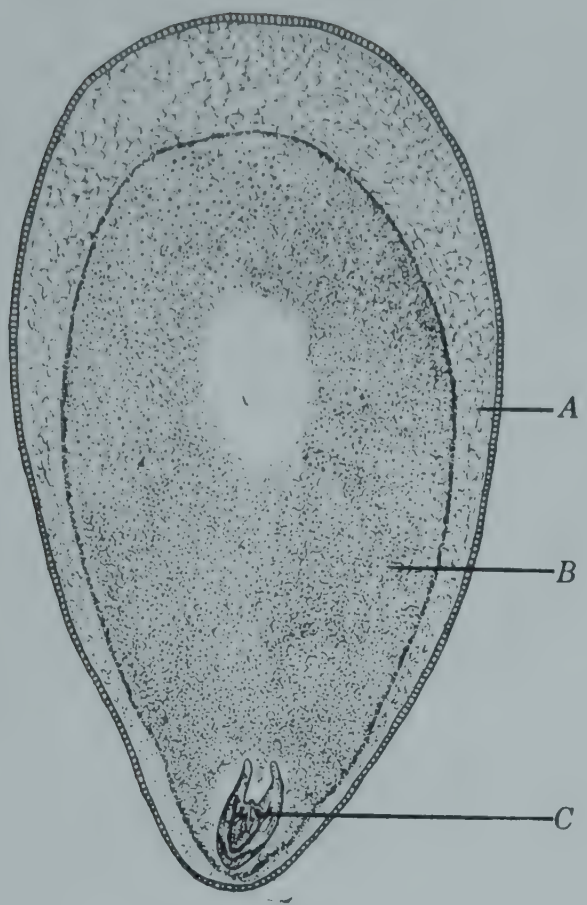
1. Development of the Hull

A better understanding of the cell structure of the spermoderm or cottonseed hull may be achieved by a résumé of its development. The spermoderm is evolved from two integuments of the ovule, which originate as products of the mother plant. From the moment of fertilization the integuments develop with great rapidity. The cell development is not uniform, however, in respect to the several layers which constitute the whole spermoderm structure. Accelerated development takes place first in the palisade cells, which attain early maturity even to their lignification. The palisade cell structure, *E* (Figs. 6a and 6b), constituting the inner epiderm of the external integument is likewise protective tissue which reaches maturity in advance of the parenchymatic tissues. The outer epiderm of the external integument, *B*, or the surface cell structure, constitutes protective tissue but does not mature with the rapidity of the palisade cells. Initially, the rapidly formed epidermal cells, *B, E, G, I,* are laden with cytoplasm, apparently without inclusions, while the more slowly maturing cells of the parenchyma contain starch grains. In the latter stages of the development of the embryo the nutrients of the spermoderm are consumed, and the starch of the parenchyma cells is replaced by sugar and oil, while the cytoplasm of the epidermal cells shows inclusions of sugars and oil. Virtually all of the nutrients of the epidermal cells are finally consumed in maturing the embryo.

In the earlier stages of development the cell wall of the spermoderm contains cellulose. Later, the lignification of the lower two-thirds of the outer epiderm of the internal integument is accomplished, as well as the complete lignification of the inner epiderm of the external integument. At maturity all of the other cell structures show tannin impregnations.

2. Proportions of the Hull

The spermoderm or cottonseed hull is by no means uniform with respect to thickness and weight in the various producing sections of the country. The weight of the hull varies between 40 and 50% of the weight of the whole cottonseed. It varies in thickness from 0.28 to 0.35 mm. Neither is the hull of a single seed uniform in thickness.



(a)



(b)



(c)

Fig. 8. Longitudinal section through a cottonseed twenty days old (a), thirty-five days old (b), mature (c); *A*, endosperm; *B*, nucellus; *C*, embryo; *D*, cotyledon; *E*, hypocotyl; *F*, epicotyl.

B. Nucellus

Close examination of a longitudinal or transverse section of a cottonseed will disclose the presence of a thin skin or membrane occurring between the inner wall of the spermoderm and the embryo. It is this membrane which forms the attachment to the cottonseed hull at the chalazal cap. The membrane is not exclusively the remnant of the nucellus of the ovule or perisperm, but is also composed of the endosperm residue. The nucellus is identified in Figure 7 as "membrane cells" (*H*). The cell structure of the nucellus membrane comprises two distinct structures. The outer structure is comprised of "fringe cells" of the perisperm,[1] while the inner structure is a tissue of well-defined cell structure, *B*, of complete continuity, containing a dense aggregation of very fine aleurone grains. There appears to be no oil whatever in these cells.

Whenever an embryo is carefully extracted from the hull of the cottonseed it will be observed to be completely enveloped in the perisperm-endosperm membrane. The perisperm and endosperm, containing protein, oil, and sugar, constitute nutritive materials for the growing embryo. At the outset of the development of the embryo these materials virtually fill the area within the hull, which develops as already stated with great rapidity. In Figure 8a is a longitudinal section of a cottonseed only twenty days old in which the embryo, *C*, is in an early stage of development and completely surrounded by endosperm, *B*, which occupies about 85% of the volume of the seed. The nucellus, *A*, or perisperm occupies the outer area between the hull and endosperm. In Figure 8b the embryo is in an advanced stage of development and the only large concentration of nucellus is at the chalazal end of the seed. The endosperm, however, is generally dispersed in between the folds of the cotyledons of the embryo. In Figure 8c the embryo development is well advanced and the perisperm-endosperm nutrients are all but dissipated. After the thirty-fifth day, when much of the nutrients of the perisperm and endosperm tissue have been exhausted, the parenchyma cells of the integuments, or seed coat, provide supplementary nutrients.

The kernel or meat of a cottonseed is an embryo which has consumed the entire reservoir of endosperm nutrients in maturing. In the case of cereal grains, such as wheat or corn, the endosperm is in excess supply to the needs of the embryo, and it is the surplus of endosperm, mainly starch, which gives commercial value and importance to such grains. Conversely, cottonseed are valuable by virtue of their high concentration of protein and oil which is produced and concentrated by the embryo at the expense of endosperm.

[1] A. L. Winton and K. B. Winton, *The Structure and Composition of Foods,* Vol. I, Wiley, New York, 1932.

C. Cottonseed Kernel

The embryo of the cottonseed, comprising two cotyledons and the axial organs, together with the enveloping membrane described in the foregoing, constitutes the parts of the seed from which oil and meal are obtained (Figs. 9 and 10).



Fig. 9. Cottonseed embryos. After the hulls are removed in the cottonseed milling operation the embryos or "meats" are recovered.



Fig. 10. Cottonseed embryos. Enveloping membrane has been removed and partly unfolded. Speckled appearance is due to innumerable pigment glands.

1. Cotyledons

The cotyledons are the principal oil- and protein-yielding elements of the embryo. The cotyledon proper (Figures 11 and 12, shown in transverse section) is comprised of investing epidermal cell tissues with respect to both ventral, *A*, and dorsal, *G*, surfaces. The epidermal tissue is comprised of a single row of polygonal cells with only slight intercellular spaces. Thin-walled mother cells of the stomata, *C*, as well as multicellular glandular hairs, *H*, are prominent on the epidermal surfaces. Directly below the ventral epiderm is a single row of parenchymatous palisade cells, *B*, easily identifiable, in which both oil and protein are stored. The location of a palisade cell tissue directly below the upper or ventral epiderm presages a dorsiventral or bifacial leaf in the growing plant. The spongy parenchyma tissue, *D*, comprising cells of an irregular circular shape

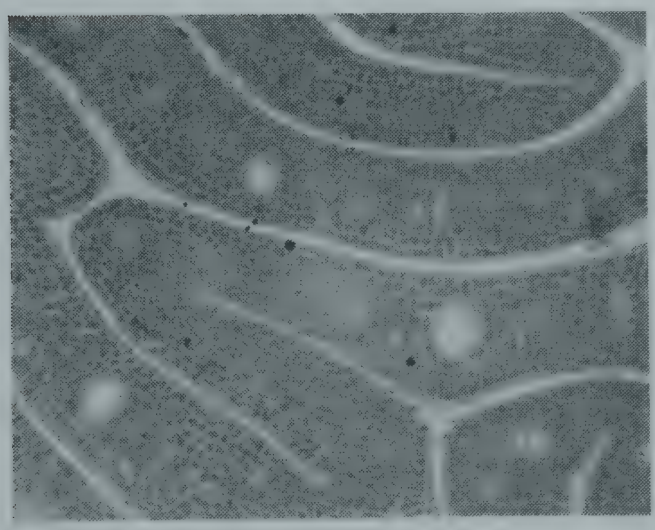


Fig. 11. Cross section of a cottonseed embryo showing how cotyledons are folded, relative size of cells, pigment glands (devoid of contents), and variations in thickness of the cotyledons.

of approximately the same size—about 8 microns—is comprised of about six superimposed layers. There are very large intercellular spaces between

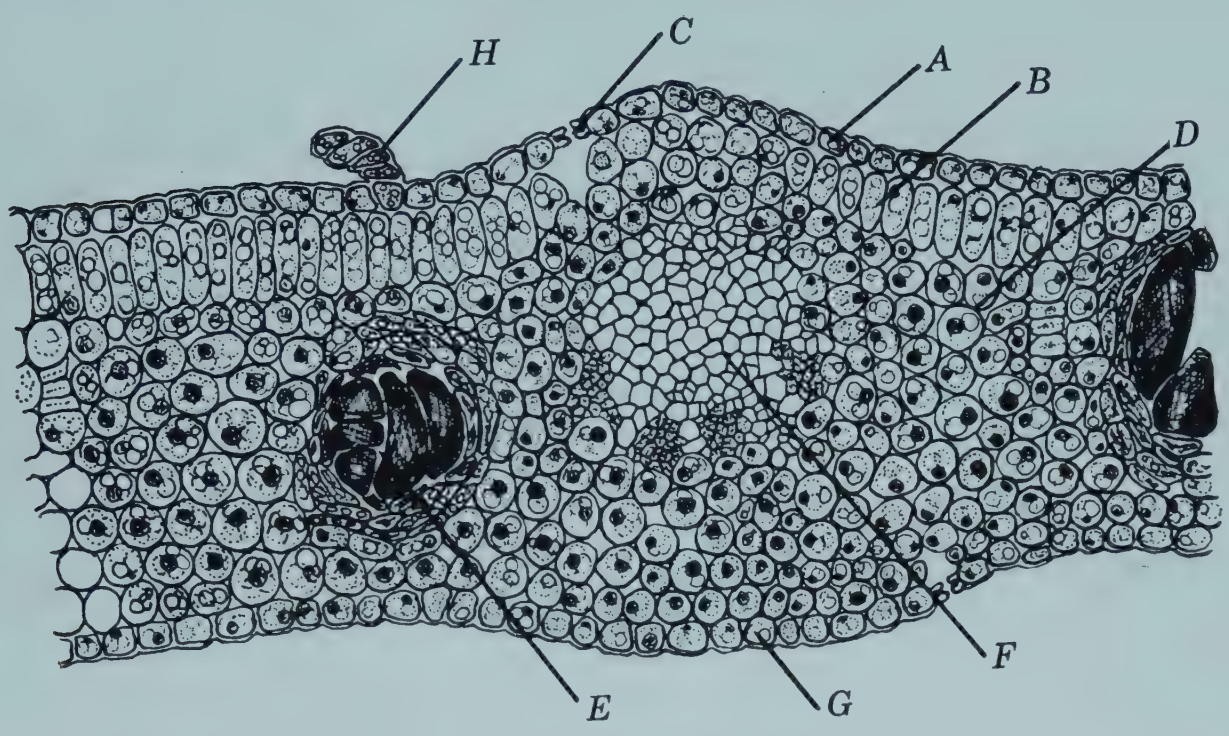


Fig. 12. Cross section through a cotyledon: *A,* upper epidermis; *B,* palisade layer; *C,* stoma; *D,* spongy parenchyma; *E,* gland; *F,* vascular bundle; *G,* lower epidermis; *H,* multicellular hair.

the cells of the parenchyma tissue. The parenchyma cells of the cotyledon contain the bulk of the oil obtainable from the cottonseed and an appreciable concentration of protein. Starch grains and crystals appear only infrequently and in widely separated cells. Vascular bundles, the future veins of the leaf, *F,* connect with the vascular system in the axial organs of the embryo. Pigment glands, *E,* are variously located, without pattern, throughout the cotyledons. The pigment glands are supported and enclosed by a double ring[1] of elongated thin-walled "mucilage cells."

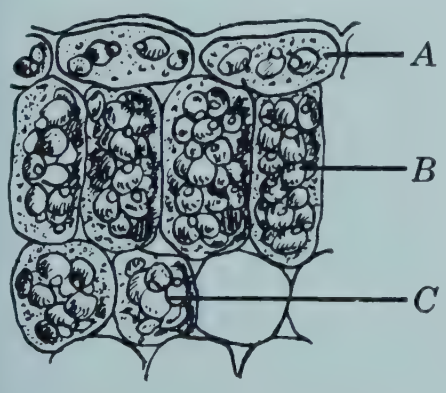


Fig. 13. Cell structure of a cotyledon: *A,* upper epidermis; *B,* palisade layer; *C,* spongy parenchyma.

Figure 13 develops by semidiagrammatic means a more detailed exposition of the cell structure of the cotyledon with respect to cell contents. Certainly the oil, in very dry cottonseed, is not observable as "free" oil. Under certain conditions of high humidity, or upon treating a section with water or solvents, oil drop-

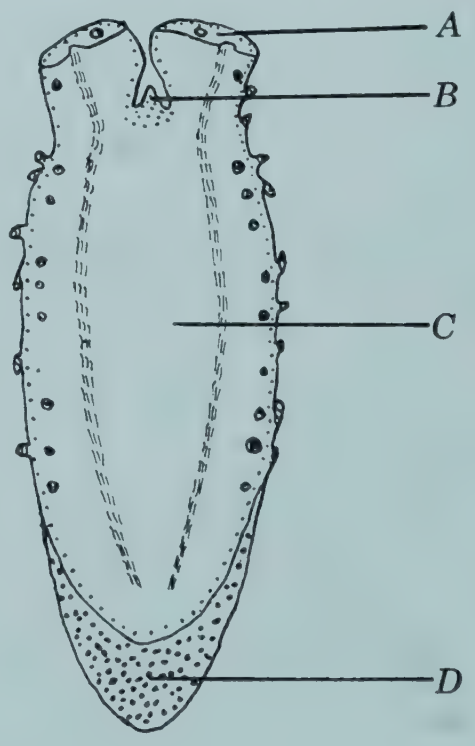


Fig. 14. Axial organs of cottonseed: *A,* surface from which cotyledons were cut; *B,* epicotyl or leaf bud; *C,* hypocotyl; *D,* root cap.

lets coalesce and appear within a cell as "free" oil. However, from the writer's observations, the oil actually appears to occur within the cell as a cytoplasmic emulsion.

2. Axial Organs

The axial organs of the embryo are developed in Figure 14. The epicotyl, *B*, and hypocotyl, *C*, form the axis of the embryo. The epicotyl is the bud from which the first true leaves are formed. The hypocotyl develops into the seedling stem and bears the cotyledons, which are not true leaves even though their basic cell structure conforms to the pattern of the true leaf structure. It is the function of the cotyledons to store nutrients necessary to support the plant through germination. The hypocotyl extends to the upper end of the elementary root. The radicle is the elementary root. The conducting bundles have their origin in the axial organs. Within the parenchyma cell structure of the axial organs, oil and protein are stored, together with starch and calcium oxalate. Also, within the spongy tissue, in the meshes of the net formed by the vascular bundles, are pigment glands (containing gossypol) which occur characteristically as in the cotyledons.

CHAPTER IV

COTTONSEED COMPOSITION—RELATION TO VARIETY, MATURITY, AND ENVIRONMENT OF THE PLANT

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I. Introduction

The relative composition of cottonseed is but one expression of a compromise between the limits of the genetic potentials of the variety and the combined stresses of environment during growth of the plant and maturation of the seed. Any one section of the cotton belt may be productive of but little variation in composition of seed because of similarity in the potentials of the varieties adapted to that region and a tendency for soils and climate to be fairly consistent throughout that particular area. But, if seed of different varieties (species or strains) are compared from growth at widely different locations and from different crop years, then the possibilities for variation in relative chemical and morphological composition of the seed are considerable.[1–5]

Variability can be related in part to differences in habit of growth and reproduction, but it (variability) can be very dependent upon adaptability of these genetic potentials to the environment.[5] On the other hand, there is considerable difference among varieties commonly grown, with respect to comparative morphological development of the seed itself. Seeds may be inherently large or small; they may produce a high percentage of short fuzz fibers (linters) or they may be found essentially naked. Seed may also differ quite widely in relative proportions of kernels and hulls.[6] To all these possibilities for variation as to habit of growth and morphology of the seed there is to be added the possibilities for

[1] A. F. Sievers and M. S. Lowman, *A Study of Cottonseed With Reference to Varietal Characteristics and Sources of Production,* mimeographed release of Bureau of Plant Industry, U.S. Dept. Agr., 1932.

[2] O. A. Pope and J. O. Ware, *U.S. Dept. Agr. Tech. Bull.,* **903** (1945).

[3] W. H. Tharp, *unpublished data.*

[4] H. B. Brown, *Cotton,* McGraw-Hill, New York, 1938.

[5] W. W. Garner, H. A. Allard, and C. O. Foubert, *J. Agr. Research,* **3,** 227–249 (1914).

[6] L. E. Rast, *Georgia State Coll. Agr. Bull.,* **121,** 19–26 (1917).

variation in the deposition of the chemical reserves in the embryo. These are storage constituents and consist predominantly of lipids (oil) and proteins. Variations in crude fiber and ash content are secondary considerations, but are important in relation to feed and fertilizer values of certain cottonseed products.[7, 8]

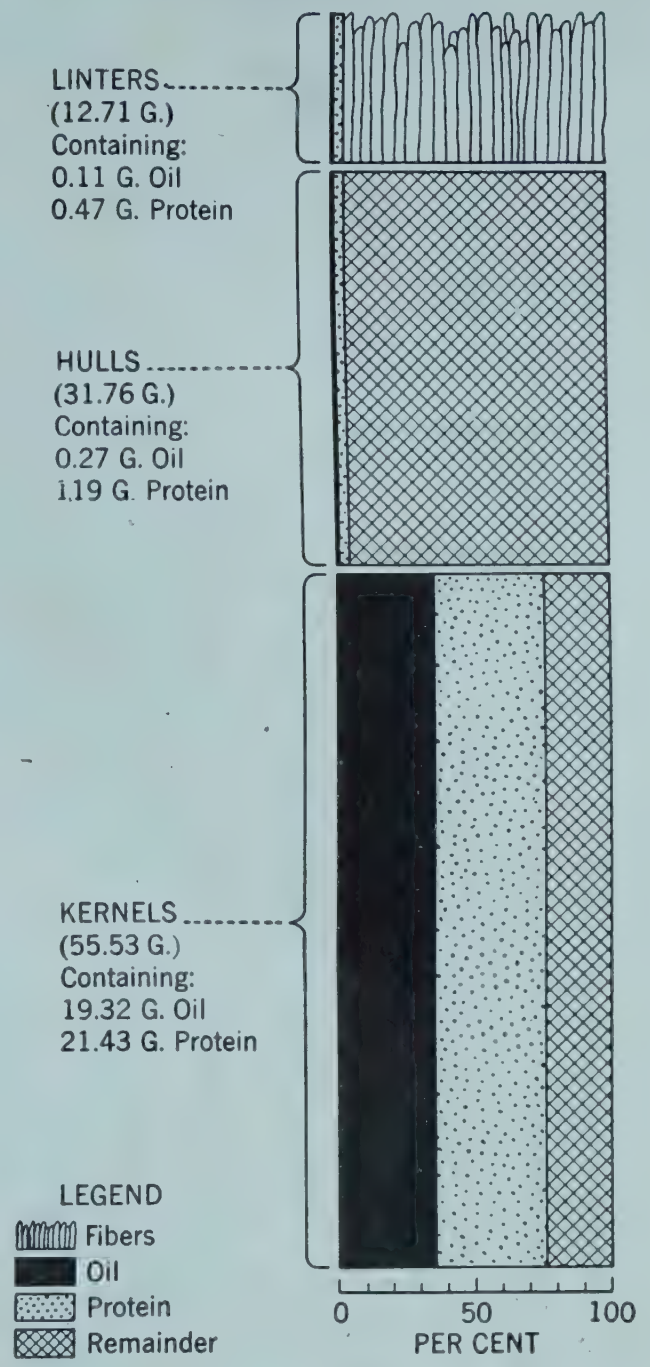
A. Basis of Measurement

The basis for measuring variability in the composition of cottonseed must be clearly defined before exact comparisons can be made between the results obtained by different analysts. There are many means of expressing the partial composition of seed, and different results may appear solely because of differences in methods of measuring the constituents and calculating the data. Statistical reports of composition are usually made on what might be considered the industrial basis. During the 1939–1940 season, for example, the mills in the United States obtained an average yield of 1,894 pounds of products per ton of seed crushed. This total was divided as follows: [9]

Product	Amount produced	
	Pounds	Per cent
Crude oil	319	15.95
Cake or meal	907	45.35
Hulls	508	25.40
Linters	160	8.00
Manufacturing loss	106	5.30
Total	2,000	100.00

The preceding division of cottonseed represents the basis on which mills sell their products. When they buy seed from gins or growers the transactions are governed by the "Rules" of the National Cottonseed Products Association [10] and the grade determines the price. If "quality" factors are disregarded for the present, the grade becomes dependent upon the percentages of oil and ammonia measured on the "as received" sample of seed (moisture being included in the base weight of the sample). This method of representing composition may be considered the "grade basis." Other methods have been adopted because investigators have chosen a basis that would facilitate clarification of the problems being

[7] C. B. Williams, *Bull. North Carolina State Board Agr.*, **27,** No. 9 (1906).
[8] H. C. White, *Georgia Expt. Sta. Bull.*, **114,** 267–268 (1915).
[9] National Cottonseed Products Association, *Cottonseed and Its Products*, 1941 ed., published by the Association, Memphis.
[10] National Cottonseed Products Association, *Rules Governing Transactions between Members,* published annually by the Association, Memphis.



Basis of calculation and measurement	Cottonseed product						
	Seed index (100 seed)	Linters (fuzz)	Kernel (meats)	Hull (fuzzy)	Oil (lipids)	Ammonia (N X 1.21)	Protein (NH_3 X 5.13)
Percentages or grams in moisture-free fuzzy seed (as illustrated)	10.00	12.71	55.53[a]	44.47[a]	19.70	4.50	23.09
Percentages in fuzzy seed with 10% moisture (Commercial)	11.11	11.44	49.97	40.02	17.73[a]	4.05[a]	20.76
Percentages in acid-delinted, moisture-free seed	8.73	0	63.62	36.38	22.44	5.05	25.91
Percentages in acid-delinted, seed with 10% moisture	9.70	0	53.86	43.13	20.20	4.55	23.32
Percentages in moisture-free kernel					34.79	7.55	38.73
Percentages in moisture-free fuzzy hull					0.85[b]	0.73[b]	3.74
Available products per ton of cottonseed at 10% moisture content					293.6 (lb.)	951.7 (lb. of 8% NH_3 cake)	
Cottonseed grade (prime quality)	100.0 points						

[a] Adjusted averages Regional Spinning Study, 1944[3]
[b] Averages from Regional Spinning Study, 1943[3]

Fig. 15. Diagrammatic representation and comparison of different bases for measuring composition of cottonseed.

studied, or in some cases because they have lacked equipment for carrying out complete analyses.

The relationship between different bases of measurement is represented in Figure 15. The illustrated example is presented on an arbitrary basis of 1,000 moisture-free fuzzy seed, with each seed weighing 0.1 gram and having an assumed morphological and chemical composition as depicted at the left of the figure. There is seldom any necessity to measure oil and nitrogen content of each tissue (fuzzy hull and kernel), but the approximate distribution of these two reserve substances should be recognized. At the right in Figure 15 the composition of seed in the example is recalculated to the "industrial" basis, to the "grade" basis, and to the several other bases most utilized by investigators. It is wished to emphasize here that, regardless of the basis used, the embryo is the only portion of the seed wherein the storage reserves are deposited in any appreciable quantity (usually better than 90% of the protein and 95% of the oil appears there) and the kernel comprises only about one-half of the entire weight of the fuzzy seed.

B. Physical Association of Lipids and Proteins

The fatty substances known as oils or lipids are apparently found in varying quantity in every living cell, and protein is the main constituent of protoplasm.[11] These two substances and certain higher carbohydrates constitute the principal storage reserves in seeds; however, only the lipids and proteins are abundant in cottonseed. The reserve lipids of cottonseed are mostly in the form of glycerides and are liquid at ordinary temperatures. Proteins are found in a dissolved state in the cell sap, but reserve proteins of the cottonseed embryo are mostly in the amorphic semicrystalline state (as aleurone grains), or in a crystalline state.[11]

The exact physical relationship between the lipids and proteins of plant cells was considered by Walker [12] to be that of minute droplets of oil distributed in the cytoplasm, but Tschirch and Kritzler [13] considered that the oil was homogenously mixed with the protoplasm. Czapek [14] reported that it was ultramicroscopically divided in the protoplasm and that the presence of oil drops could not be demonstrated. Haberlandt [15] stated that oil is usually contained in interstices in the delicate meshwork of the protoplasm but that when present only in small amounts it is suspended as droplets. Dangeard,[16] by intravital staining, found oil to be

[11] E. C. Miller, *Plant Physiology,* McGraw-Hill, New York, 1931, Chapters IX and X.

[12] J. H. Walker, *Jahrb. wiss. Botan.,* **19,** 423–496 (1896).

[13] A. Tschirch and H. Kritzler, *Ber. deut. pharm. Ges.,* **10,** 214–223 (1900).

[14] F. Czapek, *Biochemie der Pflanzen,* Fischer, Jena, Vol. 1, 1913, pp. 710–733.

[15] G. Haberlandt, *Physiological Plant Anatomy* (English translation), Macmillan, New York, 1914.

[16] P. Dangeard, *Compt. rend.,* **177,** 67–69 (1923).

in the alveoli of the cytoplasm as spherules rather than droplets, and considered these, inclusions. Policard [17] considered oil to be the continuous phase of protoplasm with it changing to the discontinuous phase during germination—the reverse occurring with development of the seeds. Pack [18] investigated seeds of the hawthorn, peach, juniper, and castor bean, finding that oil may often occur in relatively large drops. These are sometimes collected in masses which fill the meshes of the cytoplasm. In resting seeds that contain little oil it is deposited as fine drops, with dispersion increasing beyond the limits of microscopic resolution as the seeds germinate.

In mature cottonseed Reeves and Valle [19] found oil embedded in the cytoplasm as minute droplets that coalesced when fresh sections are mounted in water for observation. They stated that protein occurred in the form of aleurone grains and as a component part of the protoplasm.

C. Development of the Different Constituents

The rate of morphological development of cottonseed in relation to that of the boll, and the course of comparative changes in the chemical constituents of the two, have considerable bearing on the ultimate possibilities for variability in chemical composition of the mature seed. Many of the steps in biosynthesis within the plant have not been reproduced *in vitro* so that any one schematic representation of all the processes may be presumed to be somewhat controversial. On the other hand, certain trends are recognized and rather generally accepted. One of the more recent concepts, that of Wadleigh,[20] is illustrated in Figure 16. According to it, although the synthesis of lipids and proteins is dependent upon the total supply of carbohydrate, the steps in any comparative inter-limiting dependency would be considerably involved. A dependency of the development of lipids on the supply of some particular carbohydrate is much easier to visualize in Figure 16, but here also much of the exact evidence is lacking.

That oil could be derived from sugars was inferred from the work of DeLuca and Leclerc du Sablon, who found that the development of oil coincided with depletion and ultimate disappearance of sugars in the seed of the olive [21] and the walnut.[22] Gerber [23] studied this relationship from the standpoint of respiratory quotients of developing seed. He found that the quotient was less than unity at the highest sugar content, unity or well above while sugar was disappearing and oil being deposited, and again less

[17] A. Policard and G. Mengenot, *Compt. rend.*, **176,** 1841–1844 (1923).
[18] D. A. Pack, *Botan. Gaz.*, **79,** 334–338 (1925).
[19] R. G. Reeves and C. C. Valle, *Botan. Gaz.*, **93,** 259–277 (1932).
[20] C. H. Wadleigh, *Arkansas Agr. Expt. Sta. Bull.*, **446** (1944).
[21] S. DeLuca, *Compt. rend.*, **53,** 380–384 (1861); **55,** 470–473, 506–510 (1862).
[22] M. Leclerc du Sablon, *Compt. rend.*, **117,** 524–527 (1893).
[23] C. Gerber, *Compt. rend.*, **125,** 658–661 (1897).

than unity after the sugars had disappeared. Organic acids that would give rise to a quotient above unity were not found in the developing seeds nor was alcohol observed. He concluded from these results that oil is produced at the expense of carbohydrates in the seed. Miller [11] points out that there is considerable evidence that fats and oils are formed from carbohydrates and that fats give rise to carbohydrates during the germination of oily seeds. He emphasizes the fact that carbohydrates continue to disappear as oil increases in certain seeds detached from the plant. Hexoses have

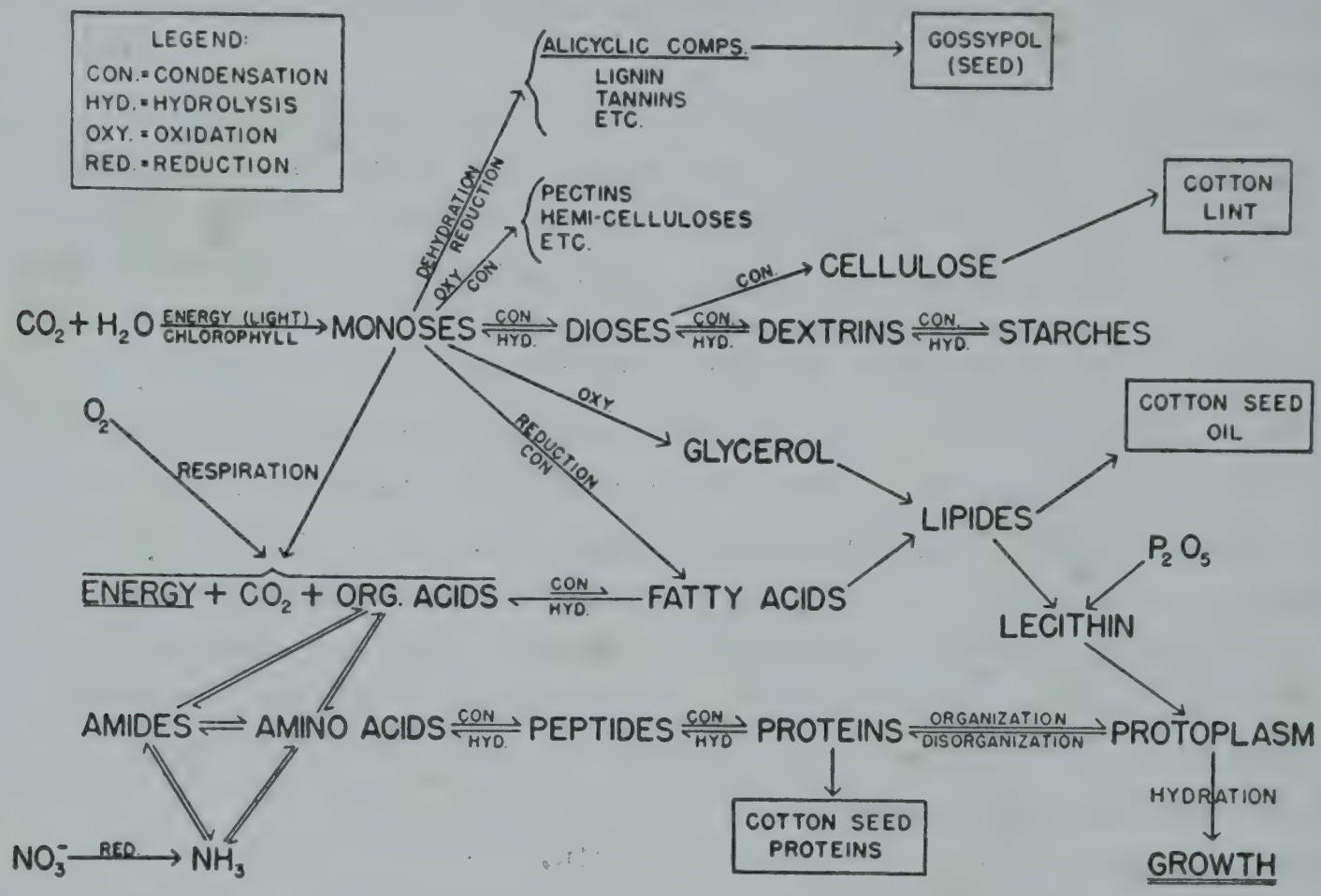


Fig. 16. Diagrammatic representation of some of the more important biochemical equilibria occurring in the cotton plant.[20]

been broken down to pyruvic acid and condensed to longer chain acids *in vitro* by Smedley [24]; however, this does not necessarily constitute evidence of a simliar process within the plant. Ivanow [25] found that in developing seed (flax, rape, hemp, and sunflower) there was a sharp decrease in the acid value of the oil and increases in saponification value and iodine value as the oil content increased. This was thought to indicate that there was a connection between carbohydrates and higher fatty acids, and that unsaturated acids were derived from saturated acids. Vallee [26] states that the particular carbohydrate transferred directly to fats and oils is not known, but according to Terroine [27] saccharose is the last one to disappear on development and the first to be detected in germination

[24] I. Smedley, *J. Physiol.*, **45,** 25–27 (1912).
[25] S. Ivanow, *Ber. deut. botan. Ges.*, **20,** 366–372 (1911).
[26] C. Vallee, *Compt. rend.*, **136,** 114–117 (1903).
[27] E. F. Terroine, *Ann. sci. nat. Botan.*, **10,** No. 26, 1–63 (1920); *Botan. Gaz.*, **75,** 224 (1923).

of oily seeds. A trisaccharide that might have been raffinose was found in embryos of developing cottonseed.[19] Starches have been found in cotton embryos at various stages of development, but only in minute quantities.[19, 28] Rainey [29] found that the development of Sea Island seed passed through two phases. The first was characterized by a high water and reducing sugar content of the ovule. During the second phase no further increase in the size of the seed occurred, but the "primary scaffolding" of sugar and water was almost wholly replaced by mature boll constituents: protein, oil, and cellulose. He found that the total fresh weight of ovules reached a maximum in five weeks, but only 15% of the oil and less than 50% of the protein and total dry matter had accumulated by this time. Certain of his data are reproduced in Table 19. In the examination of such data it should be noted that total accumulations proceed at a different rate from percentages calculated on a total dry matter basis. Wadleigh,[20] studying the effects of nitrogen supply, found that metabolic conditions characterized by an increase in nitrogenous reserves and the depletion of carbohydrates in the plant resulted in an increase in protein and a decrease in oil content of the seeds. Garner *et al.*[5] noted that carbohydrates accumulated during the vegetative period and was then transformed to oil during the reproductive period of the plants.

The specific rate and time of development of oil and protein in the cottonseed depend on both variety and environment, but comparative development has been found to conform to a rather general pattern. Lonzinger and Raskina [30] noted that oil increased rapidly up to fifty days after flowering. Protein (water-soluble) developed rapidly to thirty-five days and at a uniform rate thereafter. Crude fiber accumulated to forty days, but ash was constant after thirty-five days. Gallup [31] studied mature and immature bolls of cotton and reported an intense period of oil and gossypol formation with gossypol developing more rapidly than oil. Later he reported [32, 33] a development of both oil and gossypol at about the same rate. He felt that their development was related, with gossypol possibly acting as an accelerator for the formation of oil. He found that nitrogenous reserves were deposited early and at a continuous rate, whereas oil and gossypol had a relatively rapid period of development between twenty-four and fifty days following flowering. Sugars were found to decrease as the oil content rose from 8 to 21%. He noted a critical period of development (between twenty and thirty days) in which the production of

[28] R. G. Reeves and J. O. Beasley, *J. Agr. Research,* **51,** 935–944 (1935).
[29] R. C. Rainey, *Physiological Work, Progress Report, 1939–1940,* Empire Cotton Growing Corp., 1940, pp. 39–46.
[30] E. Lonzinger and R. Raskina, *Masloboino Zhirovoe Delo,* **17,** 57–60 (1931); *Chem. Abst.,* **26,** 3127 (1932).
[31] W. D. Gallup, *J. Agr. Research,* **34,** 897–992 (1927).
[32] W. D. Gallup, *J. Agr. Research,* **36,** 471–480 (1928).
[33] W. D. Gallup, *Oklahoma Agr. Expt. Sta. Rept.,* **4,** 178–181 (1932).

TABLE 19

Growth in the Cotton Boll in Terms of Constituents of the Developing Ovules[a]

Age, weeks	Water, g.	Reducing sugars		Oligosaccharides		Protein		Oil		Remaining dry matter, mg.	Total dry weight, mg.
		mg.	%	mg.	%	mg.	%	mg.	%		
Flowering	0.025	0.27	4.50	0.23	3.83	2.4	39.94	0.009	0.15	3.1	6.009
1	0.614	35.1	46.49	5.4	7.15	15	19.87	—	—	20	75.5
2	4.17	236	45.41	40.0	7.70	57.2	11.00	6.5	1.25	180	519.7
3	8.05	463	42.54	75.3	6.92	145.0	13.32	—	—	405	1088.3
4	10.13	433	26.32	107	6.50	206	12.52	16.0	0.97	883	1645.0
5	10.41	339	15.85	—	—	275	12.87	76.5	3.58	1445	2135.5
6	8.67	229	7.39	161	5.19	329	10.61	234.0	7.55	2147	3100.0
7	8.47	196	5.14	193	5.06	420	11.00	379.0	9.93	2627	3815.0
8	7.92	163	3.98	142	3.46	623	15.20	—	—	3171	4099.0
9	6.99	88.2	1.95	122	2.69	676	14.93	—	—	3640	4526.2
10 (splitting)	2–5	30.00	0.66	121.00	2.68	629.0	13.92	568.00	12.57	3171.0	4519.0
Significant difference 2–10 weeks (P = 0.05)	—	0.59 (2–9 weeks)	—	41	—	31	—	44	—	—	—

[a] Weights and percentages are calculated for the data of R. C. Rainey, *Physiological Work, Progress Report, 1939–1940*, Empire Cotton Growing Corp., 1940, pp. 39–46, and are listed on a dry matter basis.

oil was nearly completed, while other parts were still maturing. Caskey and Gallup [34] reported that sugars decreased in the developing cotton boll oil and gossypol increased, but they did not believe that oil was necessarily developed at the expense of sugars. Reeves and Beasley [28] examined developing ovules of cottonseed both microchemically and anatomically. A summary of the results of their work is given in Table 20. They found a rapid development in the weight of the seed up to 34–35 days. Protein and starch made their appearance in ovules on the sixth and ninth days, respectively, and traces of oil on the sixteenth day. Starch decreased gradually throughout. At eighteen days the young resin glands gave a reaction in sulfuric acid considered characteristic of gossypol. This would place initiation of oil and gossypol at about the same time.[17,19] Wadleigh [20] found the development of oil and gossypol to be affected in like manner

TABLE 20

Morphological and Chemical Changes in Cotton Embryos According to Age[a]

Morphological and chemical changes	Age, days	Embryos weighed, number	Green weight, mg.	Dry weight, mg.	Embryos measured, number	Length, mm.
Occasionally first division of zygote	1	—	—	—	—	—
First or second division of zygote	2	—	—	—	—	—
Quadrant and other similar stages	3	—	—	—	—	—
Octant; separation of dermatogen	4	—	—	—	—	—
Carbohydrates (Molisch reaction) and proteins present	6	—	—	—	2	0.07
Early organization of cotyledons and hypocotyl; appearance of histogens and starch	9	—	—	—	2	0.29
Location of embryo at side of embryo sac opposite raphe	12	—	—	—	15	1.6
Appearance in cotyledons of provascular strands, resin glands, and palisade tissue; early differentiation of plumule, appearance of oil	15	—	—	—	16	3.8
	16	20	7.5	3.0	—	—
Appearance of gossypol and pentosans	18	—	—	—	13	6.8
	19	14	16.4	4.6	—	—
Continuation of growth and differentiation of tissues that have already arisen	22	14	53.6	21.0	5	8.6
	26	20	77.8	38.0	12	9.9
	30	55	100.2	52.0	30	9.5
	32	14	107.1	60.0	29	9.6
	34	20	110.3	61.2	20	9.8
	36	59	109.8	64.7	31	9.3
	38	76	99.4	63.0	76	9.2
	40	50	90.6	70.2	50	9.2
	43	44	70.2	69.5	44	7.9
	46	30	63.5	63.3	30	8.0
	53	20	65.7	65.9	20	8.1

[a] R. G. Reeves and J. O. Beasley, *J. Agr. Research*, **51**, 935–944 (1935).

[34] C. Caskey and W. D. Gallup, *J. Agr. Research*, **42**, 671–673 (1931).

by nutritional variations and ordinal rank of blooming with a correlation coefficient of $r = 0.933$ for the association. Seale [35] reported the rapid period of oil development in Sea Island cotton to be between 25 and 40 days after flowering, with the refractive index of the oil becoming increasingly higher after the thirtieth day (Table 21).

TABLE 21

Changes in Developing Seed of Two Varieties of Sea Island Cotton at St. Vincent, B.W.I., 1939–1940[a]

Age of seed, days	Moisture in seed, %		Bolls which had split, %		Oil content of seed, %				Refractive index of oil, n_D^{20}	
					V 135		M S I			
	V 135	M S I	V 135	M S I	Referred to original weight	Referred to oven-dry weight	Referred to original weight	Referred to oven-dry weight	V 135	M S I
15	79.1	77.7	0	0	0.28	1.32	0.31	1.41	—	—
20	76.5	77.8	0	0	0.23	0.98	0.30	1.33	—	—
25	74.8	76.3	0	0	0.70	2.78	0.75	3.17	1.4763	1.4764
30	72.0	73.6	0	0	2.42	8.66	2.72	10.31	1.4737	1.4724
35	69.9	65.9	0	0	4.45	14.79	5.78	16.96	1.4737	1.4744
40	61.1	57.9	0	0	8.89	22.86	9.95	23.63	1.4754	1.4764
45	52.0	51.0	26.9	23.1	11.28	23.51	11.74	23.96	1.4750	1.4771
50	41.9	31.8	70.6	93.6	13.20	22.72	15.52	22.75	1.4745	1.4778
55	40.1	12.0	76.3	100.0	13.77	22.98	20.33	23.10	1.4759	1.4787
60	12.9	10.3	100.0	100.0	20.41	23.43	20.40	22.74	1.4763	1.4787
65	9.6	10.5	100.0	100.0	19.24	21.28	20.67	23.10	1.4773	1.4791

[a] C. C. Seale, *Trop. Agr. Trinidad*, **19**, 210–214 (1942).

Certain of these trends have a definite bearing on the possibilities for variation in composition. Of special interest is the fact that most of the increase in dry weight of the seed apparently takes place well before the bolls open. The same is true of increases in the crude fiber and ash contents. Oil (and gossypol) accumulates rapidly during the middle period of development (roughly at 25 to 45 days), whereas protein normally accumulates at a comparatively even rate throughout the period from flowering to the development of open bolls and mature seed. The sugars tend to disappear as the oil develops, but there remains about 8% of raffinose[35a] in the oil-free kernels or about 2.5% in "as received" fuzzy cottonseed.

II. Average Composition

There have been many changes in methodology at cottonseed mills, in cultural practices, and in varietal selection since the inception of the industry that is now built around cottonseed products. Wamble reports

[35] C. C. Seale, *Trop. Agr. Trinidad*, **19**, 210–214 (1942).

[35a] J. D. Guthrie, C. L. Hoffpauir, E. T. Steiner, and M. F. Stansbury, *Survey of the Chemical Composition of Cotton Fibers, Cottonseed, Peanuts, and Sweet Potatoes. A Literature Review*, Processed Release AIC–61, Southern Regional Research Laboratory, U.S. Dept. Agr., 1944, p. 20.

that from 1884 (when the first important mill was established) to 1943 the annual value of this one-time by-product has changed from zero to nearly 300 million dollars.[36] An indication of the changes occurring with advance in time is given in the excerpt from Wamble's data presented in Table 22. Most of the changes in proportionate output of the mills have been the result of increased efficiency in processing the seed. Improvement has also been made in handling of the seed, and higher yields of products may have been occasioned to some smaller extent through better cultural practice and the growing of improved varieties.

Early reports of cottonseed composition are subject to some speculation in regard to the methods of analyses and the exact strain or variety under consideration. From Table 22 it can be seen that the separation of hulls,

TABLE 22

Yields of Products of Cottonseed[a]

Product	Products per ton of cottonseed			
	Reported in 1900		Reported in 1943	
	Pounds	Per cent of total	Pounds	Per cent of total
Crude oil	282	14.10	311	15.55
Cake and meal	713	35.65	887	44.35
Linters	23	1.15	190	9.50
Hulls	943	47.15	482	24.10

[a] From the data of A. C. Wamble, *Proc. Cotton Research Congress*, **5,** 109–115 (1944).

kernels, and fuzz was incomplete in the early days of the industry. For example, McBryde[37] gives a compilation of data obtained up to 1896 (Table 23) which shows that the mills produced materials far inferior to those indicated by the analyses of contemporary experiment station workers. The mill records show what was actually being produced, and the Experiment Station records showed more nearly what *could have been produced.* That the *possible yields* of these early years are close to the *probable yields* of a later era is seen in the changes that have taken place from 1896 to 1943 (Table 22).

Complete analyses of cottonseed and each of its parts are given by McBryde[37] and many others.[7, 8, 38–44] These have been presented as

[36] A. C. Wamble, *Proc. Cotton Research Congress,* **5,** 109–115 (1944).
[37] J. B. McBryde, in "The Cotton Plant," *U.S. Dept. Agr. Expt. Sta. Bull.,* **33,** 81–142 (1896).
[38] H. C. White, *Georgia Agr. Expt. Sta. Bull.,* **108** (1914).
[39] G. S. Fraps, *Texas Agr. Expt. Sta. Bull.,* **189** (1916).
[40] G. S. Fraps, *Texas Agr. Expt. Sta. Bull.,* **247,** 15–16 (1919).
[41] J. S. McHargue, *J. Am. Soc. Agron.,* **18,** 1076–1083 (1926).
[42] K. S. Markley, *J. Am. Soc. Agron.,* **20,** 1102–1107 (1928).
[43] C. W. Botkin, *New Mexico Agr. Expt. Sta. Bull.,* **175** (1929).
[44] D. M. Musser, *J. Assoc. Official Agr. Chem.,* **22,** 420–422 (1939).

TABLE 23

Comparison of Early Yields at Oil Mills and Analysis by Experiment Station Workers[a]

Cottonseed product	Average composition, %	
	From mill records	From experiment station reports
Kernels	50, yielding:	54.22, yielding:
Oil	25	36.88
Meal	75	63.12
Hulls	50, yielding:	45.78, yielding:
Linters	2.2	27.95
Hulls	97.8	72.05
Whole seed	100, yielding:	100, yielding:
Meal	37.5	34.22
Oil	12.5	20.00
Hulls	48.9	35.78
Linters	1.1	10.00

[a] J. B. McBryde, in "The Cotton Plant," *U.S. Dept. Agr. Expt. Sta. Bull.*, **33**, 81–142 (1896).

TABLE 24

Proximate Composition and Ash Constituents[a] of Cottonseed and Derived Products[b]

Constituent	Whole seed, %	Kernels, %	Hulls, %	Meal or cake, %
Moisture	9.9	6.9	9.3	7.8
Oil	19.5	29.6	0.9	7.4
Protein (N × 6.25)	19.4	30.3	3.8	44.8
Crude fiber	22.6	4.8	46.1	9.9
Ash	4.7	6.9	2.6	5.6
N-free extract	23.9	15.4	37.3	24.5
P_2O_5	1.27	1.73	0.25	2.88
K_2O	1.17	1.14	1.02	1.77
Na_2O	0.20	—	0.02	0.29
CaO	0.25	0.16	0.18	0.43
MgO	0.55	0.78	0.26	0.95
SO_3	0.12	0.12	0.08	0.19
Fe_2O_3	0.07	0.03	0.03	0.14
Cl	0.05	0.01	—	—
SiO_2	0.06	0.05	0.05	0.27
Mn	—	0.0013	0.014	—
Cu	—	0.005	0.0014	—
Zn	—	0.032	0.002	—
S (total)	—	0.36	0.04	—
F	—	—	12–14 p.p.m.	20–31 p.p.m.
I	—	—	—	23–1420 p.p.b.

[a] Average values for air-dry materials.

[b] J. D. Guthrie, C. L. Hoffpauir, E. T. Steiner, and M. F. Stansbury, *Survey of the Chemical Composition of Cotton Fibers, Cottonseed, Peanuts, and Sweet Potatoes. A Literature Review*, Processed Release AIC-61, Southern Regional Research Laboratory, U.S. Dept. Agr., 1944, p. 20.

tabulations of "proximate constituents" of whole seed, kernels, and hulls, and also as ash or "fertilizer constituents" in each of the cottonseed fractions. One of the more recent compilations of such average results, presented by Guthrie *et al.*[45] is reproduced in Table 24. A more complete treatment of these various constituents will be found in other chapters of this book. The present chapter is directed toward an understanding of variability only in those morphological fractions and in the content of materials that can be considered of prime interest to the mills—the proportions of linters, hulls, kernels, and respective oil and protein contents of each. On the other hand, the average composition of seed would be but partly outlined if "proximate" constituents and "fertilizer" constituents were not shown. In this respect it is of particular interest to note that the above-mentioned authors caution that the values listed in Table 24 are average values, and that individual values are quite variable due to the influence of *variety,* stage of *maturity, environment* of production, and mode of processing. These are the sources of variability to be considered in the remainder of this chapter.

III. Composition of Different Varieties

American cottons are considered to be of the New World type with 26 haploid chromosomes while the Asiatic, or Old World, cottons contain but 13 haploid chromosomes.[46] The two types are genetically distinct and have probably remained so since their origin, since they are noncompatible and have no known persisting fertile hybrids.[46] The three types of cotton grown extensively in the United States—Sea Island, American-Egyptian, and American upland—are probably of American origin, coming from either native Mexico or South American parents. "Variety," in terms of currently known cotton selections, can thus mean species to a certain extent, but delimitation of these two catagories is another story. Here it is important to realize that American upland selections are mostly hybrids or blends, that American-Egyptian cottons may also be hybrids of Mexican and South American types, and that the Sea Island strains, introduced first from the Bahamas,[46] may also be of hybrid origin. When the entire list of named cultured selections is considered, it is evident that there is ample opportunity for wide difference of seed characters.

A. Linters

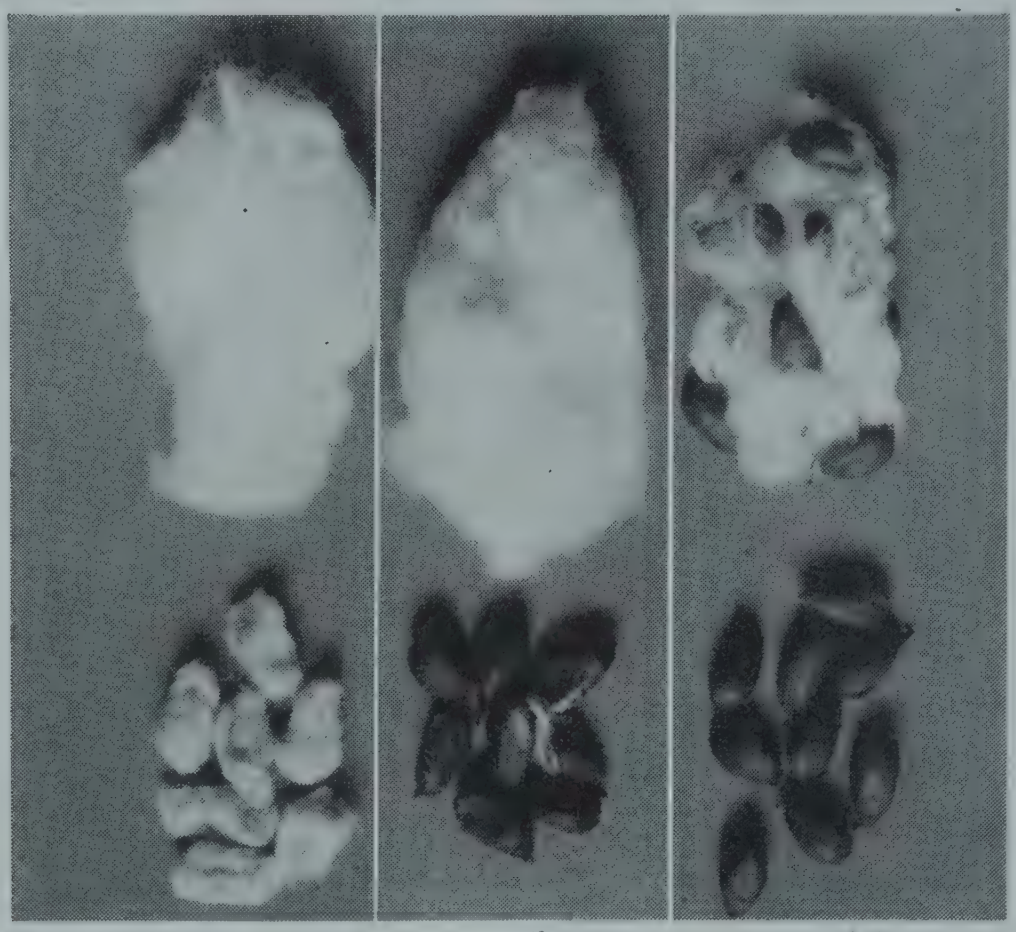
The term "linters" is used here synonomously with "fuzz" although strictly speaking the two have different meanings. The fuzz hairs are

[45] J. D. Guthrie, C. L. Hoffpauir, E. T. Steiner, and M. F. Stansbury, *Survey of the Chemical Composition of Cotton Fibers, Cottonseed, Peanuts, and Sweet Potatoes. A Literature Review,* Processed Release AIC-61, Southern Regional Research Laboratory, U.S. Dept. Agr., 1944, p. 20.

[46] J. O. Ware, *U.S. Dept. Agr. Yearbook,* 1936, 657–744.

mostly shorter, are introduced at a different time, and are morphologically distinct from the true lint fibers of cottonseed.[4] Linters usually refers to all fibers left on the seed following ginning that can be removed quantitatively and includes both lint and fuzz fibers. Writers have often used the term fuzz to denote this same removable fraction.

Differences in the inherent percentage weight of linters on cottonseed are of importance in two respects. Linters are of sufficient value as a mill product to have become the basis of an almost separate industry, so that the pounds of linters obtained per ton by the mills is of considerable concern. On the other hand, their value to the ginner and grower (those who sell the unprocessed seed) is negative in the sense that they are the



(a) (b) (c)

Fig. 17. Lock and seed of cotton: fuzzy seed parent (a); hybrid, F_1 (b); naked seed parent (c).[48]

source of a discount for an excess. This apparent anomaly results from the circumstance that the percentages of oil and ammonia in the seed are lowered by high fuzz content and it is the proportion of these that determines the grade of sound and clean cottonseed. Although no naked seed, devoid of all fibers, are as yet produced commercially, breeders have already become interested in such a possibility.[36] The seed that are marketed in this country, however, vary from the types with fuzz only on the tip, through low-fuzz content strains, up to certain selections that develop close to 20% of linters by weight.[3] The importance of variation in this portion of the cottonseed cannot be over-emphasized as long as the quantitative aspects of cottonseed grading are conditioned solely by

the percentages of oil and ammonia in the fuzzy seed. Lang [47] found that the development of fuzz (and lint) fibers followed a generally consistent course but that position and quantity patterns were dependent upon the variety or species studied. The genetic relationships for fuzzy and naked seed were worked out by Ware [48]; the characteristics of fuzzy, naked, and hybrid seed are shown in Figure 17. It is quite reasonable to expect that the nearly naked seeds might measure quite high in oil content. The inference would be in a sense misleading, however, for the mill might

TABLE 25

Average Fuzz Content of Certain Varieties of Cottonseed

National average (1935–37)[a]		Average in Mississippi Delta (1944)[b]	
Variety	Fuzz, %	Variety	Fuzz, %
Triumph 44	13.43	Delfos 531C	11.7
Dixie Triumph 759	11.59	Delfos 651	11.5
Delfos 4	14.07	Bobde	11.5
Cook 912	13.19	Stoneville 2B	12.0
Rowden 2088	18.27	Delfos 444	14.1
Half & Half	12.11	Bobshaw 1	12.4
Arkansas 17	11.85	Stoneville 2C	13.1
Startex 619	11.45	Miller	16.1
Mexican (BB)	14.86	Deltapine 14	11.0
Deltapine	13.62	Rowden (Roldo)	17.8
Acala (Rogers)	11.96	Wilds 16	11.8
Wilds 5	11.96	Coker 100–8	14.9
Stoneville 5	13.00		
Farm Relief 2	19.06		
Cleveland (W)	15.15		
Qualla	15.17		
Average	13.80	*Average*	13.2

[a] O. A. Pope and J. O. Ware, *U.S. Dept. Agr. Tech. Bull.*, **903** (1945).
[b] H. L. Thomas and F. L. Gerdes, *Cottonseed Quality Test Results of Interest to Cottonseed Oil Mill Superintendents*, mimeographed release by U.S. Dept. Agr. Marketing Service, Cotton Branch, 1945, pp. 1–9.

find that the oil and ammonia contents of the decorticated meats are of average value. Fundamentally there is no reason to expect an excess deposition of storage reserves in the embryo of a new generation because of a sparse development of hairs on the seed coat of the old or parent generation, and no exact correlation has been found among varieties for the associated variability of percentage of linters and oil and protein content of the kernels.

Selection and breeding for improvement in cotton has been, at least up to the present, guided by considerations of lint character and relative productivity. The changes made or the differences occurring in varietal capacity for fuzz production (and indeed all other seed characters) have

[47] A. G. Lang, *J. Agr. Research*, **56**, 507–522 (1938).
[48] J. O. Ware, *Arkansas Agr. Expt. Sta. Bull.*, **406**, 8 (1941).

occurred, for the most part, without intent. In fact, the goal of some seems to have been breeding the seed out of cotton because of the comparative lower value of this product. The variation in linter content of contemporary varieties has perhaps occurred more through chance than design, and yet there are quite marked differences existent (Table 25). Environment is quite an important factor in conditioning the amount of fuzz that may be produced within a given varietal potential. It is found, however, that varieties tend to hold rank throughout many environmental alterations in respect to comparative development of fuzz.[2, 3, 49]

B. Kernels and Hulls

Until recent years the oil mills bought cottonseed primarily for their kernels. The residual lint withheld valuable oil, and both linters and hull were considered merely as diluents of the cake with respect to protein content. The development of delinting and decorticating machinery was first directed toward getting rid of these unwanted products.[36] In the early days the *desideratum* was undoubtedly a high kernel content. Even today, with almost separate industries based on cottonseed hulls and linters, a seed of high kernel content is still desired for efficiency in the mill since the main products of the process are crude oil and cake or meal. A certain amount of delinted and ground hull is needed for regulation of the protein content of the cake. The remainder constitutes the lowest priced product of the mill.

Among varieties of cotton there is considerable difference as to the characteristic percentage of kernel in the seed. These differences are larger if referred to the composition of the fuzzy seed [3, 5–7, 39, 50, 51] but are also considerable when based on delinted seed.[1] Variations in the proportions of hull and kernel do not appear exactly correlated with any other seed character,[3] although high oil content of seed with high kernel content has been recognized as a definite trend.[1, 51–58] Unusually high fuzz content would condition a low percentage kernel content if other characters were comparable, but it is questionable if the percentage kernel content should

[49] H. L. Thomas and F. L. Gerdes, *Cottonseed Quality Test Results of Interest to Cottonseed Oil Mill Superintendents,* mimeographed release by U.S. Dept. Agr. Marketing Service, Cotton Branch, 1945, pp. 1–9.

[50] M. T. Harrington, *Texas Agr. Expt. Sta. Bull.,* **374,** 14–15 (1928).

[51] H. B. Brown and C. B. Anders, *Mississippi Agr. Expt. Sta. Bull.,* **187,** 9–13 (1920).

[52] C. L. Hare, *Science,* **39,** 363 (1914).

[53] S. L. Ivanov and E. I. Moshkova, *Soobshch. Biuro Chastn. Rast. Petrograd,* **2,** No. 4, 3–35 (1915); *Expt. Sta. Record,* **36,** 804 (1917).

[54] E. P. Humbert, *Science,* **40,** 411 (1917).

[55] O. F. Cook, *Science,* **48,** 167–168 (1918).

[56] L. E. Rast, *Science,* **45,** 507–508 (1917); *Georgia State Coll. Agr. Bull.,* **12,** 121 (1917); *Georgia State Coll. Agr. Circ.,* **70** (1918).

[57] E. W. Schwartze and C. L. Alsberg, *J. Agr. Research,* **25,** 285–295 (1923).

[58] A. F. Sievers, *J. Oil & Fat Ind.,* **1,** 56–61 (1924).

be based on fuzzy seed. Actually there exists a moot inference in regard to the method of expressing the kernel content of seeds as a proportion. There are but two sound morphological parts of the cottonseed: the embryo, and the seed coat with its epidermal cells elongated to form fibers (both lint and fuzz). Per cent of kernels in seed cotton becomes the sound morphological measure. Measurement of kernel proportion referred to as but a part of the whole is unlikely to be found exactly associated with any other true biological character of cottonseed. Some close correlations exist,[3] however, and their practical value is not to be discounted for lack of an ontogenetic basis.

There seems to have been no tendency for breeding and selection of cottons in this country to have improved the average kernel content of seed among those varieties most favored throughout the United States. Changes in the range and the average among some well known varieties are shown in Table 26. Differences occurring between tests are perhaps

TABLE 26

Variation among Varieties in Kernel Content of Cottonseed

Varieties	Range and average per cent kernels in seed as found by different investigations in different years							
	Williams,[a] 1906	Garner *et al.*,[b] 1914	Fraps,[c] 1916	Rast,[d] 1918	Brown and Anders,[e] 1920	Harrington,[f] 1928	Sievers and Lowman,[g] 1932	Tharp,[h] 1944
Number	21	6	20	21	25	73	15	35
Highest value	62.04	59.10	59.10	61.66	59.17	56.09	65.53[i]	59.31
Lowest value	53.34	55.70	51.20	56.68	51.74	45.18	60.84[i]	51.27
Average value	57.40	57.65	54.26	58.08	55.96	50.21	63.29[i]	55.37

[a] C. B. Williams, *Bull. North Carolina State Board Agr.*, **27**, No. 9 (1906).
[b] W. W. Garner, H. A. Allard, and C. O. Foubert, *J. Agr. Research*, **3**, 227–249 (1914).
[c] G. S. Fraps, *Texas Agr. Expt. Sta. Bull.*, **189** (1916).
[d] L. E. Rast, *Georgia State Coll. Agr. Bull.*, **121**, 19–26 (1917).
[e] H. B. Brown and C. B. Anders, *Mississippi Agr. Expt. Sta. Bull.*, **187**, 9–13 (1920).
[f] M. T. Harrington, *Texas Agr. Expt. Sta. Bull.*, **374**, 14–15 (1928).
[g] A. F. Sievers and M. S. Lowman, *A Study of Cottonseed With Reference to Varietal Characteristics and Sources of Production*, mimeographed release of Bureau of Plant Industry, U.S. Dept. Agr., 1932.
[h] W. H. Tharp, *unpublished data.*
[i] Based on acid-delinted seed.

more attributable to the methods of referring percentages than they are indicative of any progressive change (with time) in kernel content among the better adopted varieties. In the data from Sievers and Lowman,[1] for example, the percentages are referred to delinted seed rather than to the fuzzy seed basis. It must be recognized here also that between-test differences may have been occasioned almost entirely by variations in environmental factors.

C. Oil and Protein Content of Kernels

There exist three separate means of expressing the oil and protein content of cottonseed kernels, and perhaps the exact characteristic of a variety as to composition of seed is only clarified by means of all three measurements. (*a*) Oil content and protein content may be measured separately; (*b*) the sum of these percentages may be considered as the percentage "reserve capacity"; (*c*) the ratio of per cent oil to per cent protein can be used to indicate which storage product predominates. Unfortunately, there is no single one of these three means of expressing chemical content of kernels that will, without further computation, give the characteristics shown by all three.

In any large series of varieties there may be a difference of as much as 5% in the oil content of the kernels and a little greater difference in percentage protein content (Table 27). Within such a series the percentage

TABLE 27

Varietal Differences in Composition of Cottonseed Kernels

Source of data	Oil content, %	Protein content, %	Reserve capacity, %	Oil-to-protein ratio, %
Brown and Anders[a] (25 varieties)				
Lowest	31.91	31.14[b]	67.46[c]	0.88[d]
Highest	36.63	37.19[b]	71.16[c]	1.18[d]
Mean	34.67	34.19[b]	69.16[c]	1.005[d]
Standard deviation	±1.08	±1.39	±0.63	±0.072
Sievers and Lowman[e] (15 varieties)				
Lowest	34.74	39.24	77.47	0.81
Highest	38.35	44.68	79.93	0.98
Mean	36.74	41.96	78.69	0.877
Standard deviation	±1.02	±1.35	±0.82	±0.050
Tharp *et al.*[f] (22 varieties)				
Lowest	33.13	32.63	68.98	0.83
Highest	38.22	38.63	73.77	1.17
Mean	35.37	35.92	71.29	0.985
Standard deviation	±1.78	±1.51	±1.33	±0.087

[a] H. B. Brown and C. B. Anders, *Mississippi Agr. Expt. Sta. Bull.*, **187**, 9–13 (1920). Data are on an "as received" basis, but moisture content was measured, averaging 7.56%.

[b] Calculated by the author from per cent NH_3 in kernels.

[c] Calculated by the author as per cent oil in kernels plus per cent protein in kernels.

[d] Calculated by the author as per cent oil in kernels divided by per cent protein in kernels.

[e] A. F. Sievers and M. S. Lowman, *A Study of Cottonseed With Reference to Varietal Characteristics and Sources of Production*, mimeographed release of Bureau of Plant Industry, U.S. Sept. Agr., 1932. Data are on a moisture-free basis.

[f] W. H. Tharp, *unpublished data*. Calculated to a 10% moisture.

"reserve capacity" will vary to a lesser degree, but one may find considerable deviation in the oil-to-protein ratio. The manner in which all three means of measuring oil and protein content are related among varieties has not been studied extensively. Preliminary attempts [3] to find significant correlative variation among these three measures have thus far met with failure. On the other hand, there is a certain amount of associated variability as to percentage oil content with percentage protein content in kernels (Table 28). In those studies examined,[1, 3, 6, 7, 39, 51] the

TABLE 28

Associated Variation in Oil and Protein Content of Cottonseed Kernels as Influenced by Variety

Varieties and characters	Values of r obtained in the data from different investigators[a]						
	Williams[b]	Fraps[c]	Rast[d]	Brown and Anders[e]	Sievers and Lowman[f]	Tharp[g]	
						Stoneville, Miss., 1943	Sacaton, Ariz., 1943
Varieties	21	20	21	25	15	22	17
Correlated characters: oil in kernels and nitrogen in kernels, %[h]	−0.439[i]	−0.768[j]	−0.776[j]	−0.761[j]	−0.798[j]	−0.687[j]	−0.693[j]

[a] Calculated from the published data by the author.
[b] C. B. Williams, *Bull. North Carolina State Board Agr.*, **27,** No. 9 (1906).
[c] G. S. Fraps, *Texas Agr. Expt. Sta. Bull.*, **189** (1916).
[d] L. E. Rast, *Georgia State Coll. Agr. Bull.*, **121,** 19–26 (1917).
[e] H. B. Brown and C. B. Arders, *Mississippi Agr Expt. Sta. Bull.*, **187,** 9–13 (1920).
[f] A. F. Sievers and M. L. Lowman, *A Study of Cottonseed with Reference to Variety Characteristics and Sources of Production*, mimeographed release of Bureau of Plant Industry, U. S. Dept. Agr., 1932.
[g] W. H. Tharp, *unpublished data.*
[h] Variously reported as N_2, NH_3, or protein, by the different workers.
[i] Significant, 5% level.
[j] Highly significant, 1% level.

values for the simple correlation coefficient r fell between −0.439 and −0.798, all being significant. The varietal estimates in each of these cases were drawn from sufficient replications (blocks, locations, and years) to eliminate sampling as a reason for not obtaining a more exact correlation. It must be considered, therefore, that these are significant trends but are far from perfect negative associations. This of course permits of varieties being higher or lower in both components. Having such differences in both reserve products would condition differences in percentage reserve capacity, but the capacity could also vary merely with one component being high or low and the other average.

TABLE 29

Oil and Protein Content of Seed of Different Varieties of Cotton Growth at College Station, Mississippi, 1917[a]

Variety	Meats or kernels, %	Hulls, %	Moisture in seed, %	Oil in meats, %	Oil in seed, %	Total oil per ton, gallons	Ammonia in meats, %	Ammonia in seed, %	Available oil per ton in clean seed, gallons	Cake per ton from clean seed, pounds	Hulls and linters per ton from clean seed, pounds	Length of lint, inches	Lint, %
Dodd's Prolific	59.06	40.94	7.89	35.19	20.78	55.40	6.68	3.95	47.98	1128.52	511.63	1 1/16	30.4
Trice 271-43	55.50	44.50	7.45	34.00	18.87	50.31	6.64	3.69	42.45	1054.23	627.40	1 1/16	29.0
Trice 270-41	57.00	43.00	7.79	33.90	19.32	51.51	6.85	3.90	43.20	1114.23	561.77	1 1/8	30.6
Wannamaker Cleveland	51.74	48.26	7.94	33.91	17.55	46.79	6.98	3.61	39.10	1031.38	675.37	1	35.6
Cleveland Big Boll	54.64	45.36	7.92	32.80	17.92	47.77	7.25	3.96	39.33	1130.37	573.65	1 1/16	33.2
Cleveland 641	56.50	43.50	7.21	34.29	19.37	51.64	6.99	3.95	43.22	1128.52	547.33	1	34.3
Cleveland 43	56.73	43.27	8.16	35.14	19.93	53.13	6.71	3.81	45.00	1089.50	572.86	1 1/8	32.6
Cook 919	55.74	44.26	7.67	35.06	19.54	52.09	6.72	3.75	44.10	1071.38	597.87	1	38.4
Miller	53.31	46.69	7.26	31.91	17.01	45.35	6.93	3.69	37.49	1054.23	664.58	1 1/8	33.4
Rowden	55.50	44.50	6.91	35.43	19.66	52.41	6.54	3.63	44.67	1037.09	627.88	1 1/8	33.4
Lone Star 15	54.50	45.50	7.83	33.93	18.49	49.29	7.19	3.92	40.94	1119.94	573.01	1 1/8	35.8
Lone Star 132	57.50	42.50	7.78	34.90	20.07	53.51	6.69	3.85	45.30	1099.95	560.30	1 1/8	28.4
Lone Star × Express	54.00	46.00	7.57	36.06	19.47	51.91	6.25	3.38	44.71	965.67	699.00	1 1/8	31.5
Express 412	53.60	46.40	7.99	33.81	18.12	48.31	6.89	3.69	40.45	1054.23	642.39	1 3/16	28.3
Express 122-433	56.00	44.00	7.39	35.11	19.66	52.41	6.71	3.75	44.42	1071.38	595.47	1 3/16	28.9
Express 314	55.50	44.50	7.74	34.04	18.89	50.36	6.83	3.79	42.28	1082.80	600.10	1 1/8[b]	29.0
Express 432	55.66	44.34	7.70	34.19	19.03	50.73	6.62	3.68	42.89	1051.38	626.94	1 3/16	31.7
Express 350	57.50	42.50	7.30	33.84	19.46	51.88	6.81	3.92	43.53	1119.94	553.58	1 3/16	28.0
Polk	59.17	40.83	7.75	36.63	21.67	57.77	6.07	3.59	50.12	1025.66	598.44	1 3/16	29.4
Kekchi	55.00	45.00	6.76	36.07	19.84	52.89	6.84	3.76	44.88	1074.23	589.17	1 3/16[b]	31.8
Foster 120	55.80	44.20	7.52	35.02	19.54	52.09	6.61	3.69	44.23	1054.23	614.04	1 3/16	30.9
Foster 120-449	57.50	42.50	7.67	34.69	19.95	53.19	6.88	3.96	44.75	1131.37	533.00	1 3/16	31.7
Columbia (U.S.D.A.)	56.00	44.00	6.89	34.94	19.57	52.17	6.69	3.75	44.19	1071.38	597.19	1 1/4	28.1
Columbia (Sherard's)	57.50	42.50	7.56	35.84	20.61	54.95	6.28	3.61	47.26	1031.38	614.17	1 3/16[b]	28.2
Sunflower	58.00	42.00	7.38	36.04	20.90	55.72	6.46	3.75	47.73	1071.38	570.64	1 3/8	28.0

[a] H. B. Brown and C. B. Anders, *Mississippi Agr. Expt. Sta. Bull.*, **187,** 9–13 (1920).
[b] Full.

D. Composition of Fuzzy Cottonseed

The quantity factor in cottonseed grading is determined only by the percentages of oil and ammonia in the moisture-containing sample as received by the official analyst.[10] Trash is seldom present in experimental samples and moisture-free values are employed, so that values in the official records may be found lower than values obtained by experiment station workers for comparable varieties. In either case, the percentages, or per-seed weights, of fuzz, delinted hull, and kernel, and also the exact distribution of oil and nitrogen in these parts of the seed are all lost sight of, or confused in the combined measurements. The influence of these partial composition factors has already been discussed (pages 129–136), yet if each of these variations is not compensated by one or more others, then large differences may be expected among varieties as to percentages of oil and/or ammonia content of fuzzy cottonseed.

It has long been recognized [59–63] that differences exist among varieties

TABLE 30

Average Composition of Seed from 16 Varieties of Cotton Grown at 16 Locations in 1935 and 1936[a]

Variety	Oil, %	Protein, %	Wt. 100 seeding, g.	Fuzz, %	Capacity[b]	Gin out-turn, %
Triumph 44	23.36	23.15	10.46	13.43	46.51	34.2
Dixie Triumph 759	23.07	22.12	10.06	11.59	45.19	33.9
Delfos 4	22.93	23.08	10.25	14.07	46.01	34.3
Cook 912	22.84	22.67	9.77	13.19	45.51	34.0
Rowden 2,088	22.61	23.17	12.48	18.27	45.78	33.6
Half & Half	22.57	24.79	9.62	12.11	47.36	43.5
Arkansas 17	22.52	22.43	11.20	11.85	44.95	32.0
Startex 619	22.43	23.33	11.23	11.45	45.76	35.7
Mexican (BB)	22.35	23.50	12.34	14.86	45.85	34.3
Deltapine	22.14	23.58	9.73	13.62	45.72	39.4
Acala (Rogers)	22.01	22.95	11.99	11.96	44.96	36.1
Wilds 5	21.80	22.88	12.70	11.96	44.68	31.5
Stoneville 5	21.77	22.50	9.51	13.00	44.27	36.8
Farm Relief 2	21.10	23.74	12.83	19.06	44.84	34.8
Cleveland (W)	21.00	23.09	10.93	15.15	44.09	35.4
Qualla	20.03	22.99	12.51	15.17	43.02	38.8
Average	22.16	23.12	11.10	13.80	45.28	35.5
Range	3.33	2.67	3.32	7.61	4.34	12.0

[a] O. A. Pope and J. O. Ware, *U.S. Dept. Agr. Tech. Bull.*, **903** (1945). From data on acid-delinted seed, moisture-free basis.

[b] Equal to per cent oil plus per cent protein in the seed; calculated by the author.

[59] See footnotes, this chapter, 1–3, 7, 31, 39, 43, 49–55, 57, 58.

[60] H. P. Cooper and J. H. Mitchell, *Expt. Sta. Record*, **66,** 629 (1932).

[61] J. O. Ware, *Arkansas Agr. Expt. Sta. Bull.*, **203,** 7 (1926); **215,** 8, (1926); **221,** 58–59 (1927); **268,** 34–35 (1931); **297,** 12–13 (1934).

[62] M. I. Smirnova, *Bull. Applied Botany Genetics Plant Breeding U.S.S.R.*, **Ser. III,** No. 15, 227–240 (1936), summary in English on p. 240.

[63] N. T. Hancock, *Tennessee Agr. Expt. Sta. Circ.*, **79** (1942).

as to comparative oil and nitrogen content of ginned seed. Some investigators have presented comparative data on the basis of oil and ammonia content of the kernel [1, 5, 7, 39, 51, 56, 57] and a few have shown various means of expressing the content of the same varieties.[3, 51, 56] The series [51] shown in Table 29 is of particular interest because of the inclusion of many characters and different measures of oil and nitrogen content. These results are indicative of but a single environment of growth. Averages [2] that have resulted from three-years growth at many locations are presented in Table 30. These indicate expected performance and comparative

TABLE 31

Average Composition of Seed from 12 Varieties of Cotton Grown at 6 Locations in the Mississippi Delta, 1944[a]

Variety	Averages for all locations[b]				
	Oil content, %	Ammonia content, %	Grade, points[c]	Value per ton, dollars	Residual lint (fuzz), %
Delfos 531C	20.5	3.71	109.0	61.18	11.7
Delfos 651	20.4	3.71	109.0	60.99	11.5
Bobdel	19.9	3.73	107.0	59.97	11.5
Stoneville 2B	19.5	3.71	105.0	58.85	12.0
Delfos 444	19.7	3.51	105.0	58.66	14.1
Bobshaw 1	19.4	3.67	104.5	58.57	12.4
Stoneville 2C	19.2	3.69	104.0	58.29	13.1
Miller	18.5	3.76	101.5	56.76	16.1
Deltapine 14	18.6	3.83	102.5	57.26	11.0
Rowden (Roldo)	17.7	3.74	98.5	55.16	17.8
Wilds 16	18.8	3.85	103.0	57.73	11.8
Coker 100-8	17.6	3.71	97.5	54.60	14.9
Average	19.1	3.72	104.0	—	13.2

[a] H. L. Thomas and F. L. Gerdes, *Cottonseed Quality Test Results of Interest to Cottonseed Oil Mill Superintendents*, mimeographed release by U.S. Dept. Agr. Marketing Service, Cotton Branch, 1945, pp. 1–9.

[b] Calculated on the basis of fuzzy seed at a 12% moisture content.

[c] According to N.C.P.A. Trading Rules.

differences on a nation-wide scale. A further series [49] is included in Table 31 from a study made in 1944 at six locations in the Mississippi Delta where the grade of cottonseed is usually relatively high.[64] In these last two studies the averages do not give the entire information. In the regional variety study,[2] for example, the varieties tended to hold rank with respect to most seed characters in a general way but years, locations, and years at locations often had considerable interactive influence on the rank of varieties with respect to the characters studied.

[64] M. Gieger, *J. Agr. Research*, **63**, 49–54 (1941).

E. Heredity and Miscellaneous Correlations

Attempts to improve the oil and/or protein content of cottonseed by selection have shown that a certain amount of segregation occurs in this respect even in what might be considered relatively pure parent lines.[39, 49, 54, 61] Distinct differences in oil content among progeny from a single parent have been selected, but segregation within the parent line was usually of equal magnitude. Cook [55] reports that Bain and Anders failed to find differences sought for a sound basis of selection. Fraps [39] found selections from the same parent strain to differ as much as 2.95% in protein in kernels, 5.84% in oil in kernels, and 7.9% in kernels in seed. The highest selection as to per cent kernels had the highest oil content and a low (but not the lowest) protein content. Ware,[61] after ten years of selection, found a lower oil content than in the parents only with an increased tendency toward a negatively associated variation of oil and protein content. Humbert [54] concluded from results of several years selection that divergent "biotypes" could be produced from a single variety of cotton with respect to oil and protein content of seed. This view has been held by others.[1, 49] Wamble [36] reports that considerable progress has been made in such selections within recent years, although data on the magnitude of such improvements are not available. That such divergent strains are not now available is perhaps because breeding and improvement have been directed toward the improvement of lint yield and lint character. Where progeny from single parent lines were examined for seed characters, although selection was for other reasons, it was found [49] that no new strains of a high-oil-content variety were higher than the parent, but most selections from the low-oil variety were higher than the parent. On the other hand, certain selections made by Webber [65] seem to be superior—not only in oil but in nitrogen content as well—so that definite progress is apparent along this line of investigation.

The actual mode of inheritance of oil or nitrogen content of cottonseed has not been worked out, although other quantitative and qualitative seed characters are found inherited in definite ratios.[48, 66] The latter are principally degree of nakedness or fuzziness and seed size. On the other hand, many suggestions have been made as to probable covariability in regard to oil content and other seed characters among varieties. The tendency toward an inversely associated variability for oil and nitrogen content of seed has long been recognized,[3, 43, 49, 51, 52, 57, 63] but some investigators [1, 2, 7] have disclaimed such a related variability. Large seed and high oil content have been reported as associated characters,[55] although

[65] H. H. Webber in collaboration with J. W. Neeley and W. H. Tharp, *unpublished results.*

[66] J. O. Ware, *U.S. Dept. Agr. Yearbook,* 1936, 741–743.

others have felt that small seed produced more oil,[51] whereas still others report that there is no association at all.[2, 3, 5, 50, 58] High kernel content appears to be associated with high oil content of seed among varieties,[1, 51, 55, 56, 58] but here the relationship is dependent on other characters or on the basis of measurement and may not always be found consistent.[3] Oil and gossypol content seem to be positively related characters.[31–34, 57] Oil and per cent lint are reported both as positively [7, 52] and

TABLE 32

Measurement of Cottonseed Characters among Different Series of Varieties

Pairs of characters	Values calculated for the simple correlation coefficient in the data presented by different investigations[a]				
				Tharp[e]	
	Brown and Anders[b] (25 selections)	Schwartze and Alsberg[c]	Sievers and Lowman[d] (15 selections)	Stoneville, Mississippi, 1943 (22 selections)	Sacaton, Ariz., 1943 (18 selections)
Oil in seed — NH_3 in seed	0.0172	—	−0.4612	−0.162	−0.541
Oil in seed — kernels in seed	0.8712[f]	—	0.8680[f]	0.732[f]	0.786[f]
Oil in seed — fuzz on seed	—	—	—	−0.507[f]	−0.677[f]
Oil in seed — seed weight	—	—	—	−0.004	−0.113
NH_3 in seed — kernels in seed	—	—	—	0.365	−0.031
NH_3 in seed — fuzz on seed	—	—	—	0.349	−0.059
NH_3 in seed — seed weight	—	—	—	−0.065	0.271
Kernels in seed — fuzz on seed	—	—	—	−0.824[f]	−0.911[f]
Kernels in seed — seed wt.	—	—	—	−0.042	0.105
Fuzz on seed — seed weight	—	—	—	0.066	0.294
Oil in kernels — NH_3 in kernels	−0.7608[f]	−0.82, ±0.04	−0.7984	−0.687[f]	−0.693[f]
Oil in kernels — kernels in seed	0.5055	—	0.8692[f]	0.367	0.233
NH_3 in kernels — kernel in seed	—	—	—	−0.256	−0.556[f]
Oil in kernels — seed weight	—	—	—	0.023	−0.161
Oil in kernels — fuzz on seed	—	—	—	−0.164	−0.192
NH_3 in kernels — fuzz on seed	—	—	—	−0.151	0.433
Per cent lint — oil in seed	−0.4055	—	—	—	—
Per cent lint—kernels in seed	−0.4534	—	—	—	—
Oil in kernels — gossypol in kernels	—	0.74, ±0.03	—	—	—
NH_3 in kernels — gossypol in kernels	—	−0.68, ±0.04	—	—	—

[a] Correlations calculated from published data by the author.
[b] H. B. Brown and C. B. Anders, *Mississippi Agr. Expt. Sta. Bull.*, **187**, 9–13 (1920).
[c] E. W. Schwartze and C. L. Alsberg, *J. Agr. Research*, **25**, 285–295 (1923).
[d] A. F. Sievers and M. S. Lowman, *A Study of Cottonseed With Reference to Varietal Characteristics and Sources of Production*, mimeographed release of Bureau of Plant Industry, U.S. Dept. Agr., 1932.
[e] W. H. Tharp, *unpublished data.*
[f] Highly significant, 1% level.

negatively related,[49] with others disclaiming any covariability.[2, 52] Per cent of fuzz seems to bear no relationship to oil among varieties.[2, 3, 49] From still other studies it appears that high oil content may be related to the content of inorganic constituents,[52] to large bolls,[52] to tensile strength of the lint,[7] and to shortness of staple,[52] but bears no relationship to lint quality [49] or to quality of the oil.[50]

A great many correlative associations among cottonseed characters have been evaluated statistically,[67] particularly in relation to seed size and seed fuzziness. The evaluation of the association of oil and protein content of seed with other cottonseed characters have been presented in but few instances.[3, 57, 63] The correlative variation of oil and protein in the kernel on a per cent basis (Table 32) is seen to be more consistently associated than when the association is based on percentages in the fuzzy seed. On the seed basis the generally nonassociated variability in percentages of kernels and hulls are the influences contributing to lack of correlation. For the same reasons the per cent oil in seed seems associated with per cent kernels in seed in a positive manner, but this relationship will be found nonsignificant in certain series of selections.[3] It is, however, a rather logical trend, since comparative reduction in either delinted hull or fuzz, or both, would automatically tend to produce a higher oil and protein content of cottonseed, other characteristics remaining constant. In consideration of the seed characters alone (lint excluded) there would appear little possibility of increasing percentages of fuzz in the seed as well as percentages of oil unless the percentage of delinted hull is lowered by selection or breeding; such an alteration which would allow a higher content of both components. The ratio of oil to nitrogen content of the kernel is perhaps the most important character for consideration of the breeder,[63] but the proportion of delinted hull to kernel can hardly be ignored. Undue reduction of the fuzz content of the seed would seem a poor breeding objective. It might allow for increased percentages of oil and protein in the seed (considering their percentage content in the kernel unaltered), but at current comparative prices for the products there would be little, if any, increased value to the oil mills.

IV. Geographic Source and Weather

Location, season, and weather are so interrelated as to their influence on variability in composition of cottonseed that it is often difficult to discuss one source without including one or both of the remaining sources of influence. This is particularly true where information has been based on oil mill records and official chemist's reports. In these cases [37, 39, 56, 68–75]

[67] These have been reviewed by H. B. Brown, see footnote 4, p. 117.
[68] C. F. Cresswell and B. L. Bidwell, *U.S. Dept. Agr. Tech. Bull.*, **948** (1921).
[69] G. S. Jamieson and W. F. Baughman, *Cotton Oil Press*, **4**, 85–87 (1920).

the seed are almost never identified as to variety, the sample may have been blended from many different but adjacent localities, and often the mill may have received seed from outside the state in which it is located. These analytical reports, however, allow for a study of trends that, because of the volume represented by each sample and the number of samples analyzed, have some elements of reliability lacking in more precise experiments [1-3, 5, 39, 43, 57, 63] where deductions must be drawn from analysis of fewer samples of small size.

A. Quantitative Composition

The general trend of variation in quantitative composition of seed throughout the cotton growing areas in the United States has been shown [1-3, 68] to be as follows:

The irrigated West (California, Arizona, New Mexico, and certain Texas valleys) produces well filled seed of the highest oil content in the United States and very high protein content.

In the arid Southwest (Texas, Oklahoma, and some of western Arkansas) the seed are often poorly filled with kernels, and have a high percentage of protein with a low oil content.

In the mid-south group of states (eastern Arkansas, western Tennessee, Mississippi and Louisiana—particularly the Mississippi Delta region) the oil content of seed tends to be high and the protein content, medium to low in fairly well filled seed.

In the southeastern area (eastern Tennessee, North Carolina, South Carolina, Georgia, Alabama, and Florida) the average oil content is second only to that in the western irrigated region, and the protein content is medium to low in fairly well filled seed.

The northern tier of states (Missouri, Kentucky, and Virginia) produce very little cottonseed, but such as is produced has been reported as being high in oil and low in protein content.

Differences in cottonseed composition induced by season need to be stated in terms of location-year. Variability from one year to the next at one location bears no exact relationship to variability between the same years in another widely separated test area.[1-3] Locations must be tested several years before a location estimate can be established and many such location-year averages should be combined [68-70] to allow for a reliable

[70] H. J. Morrison and L. W. Bosart, *J. Oil & Fat Ind.*, **3,** 130–134 (1926).
[71] T. C. Law, *Cotton Oil Press,* **2,** 41–44 (1918).
[72] G. S. Meloy, *J. Oil & Fat Ind.*, **4,** 307–314 (1927).
[73] G. S. Meloy, *Variations in Composition and Grade of Cottonseed Produced in the States of Arkansas, Louisiana, Mississippi, and Tennessee, Seasons of 1934–35 to 1937–38,* processed report by U.S. Dept. Agr. Marketing Service, 1939.
[74] G. S. Meloy, *Cotton and Cotton Oil Press,* **44,** No. 23, 14–16 (Nov. 6, 1943).
[75] G. S. Meloy, *Cotton and Cotton Oil Press,* May 17–18, 1944.

estimate of the trend in composition associated with geographical source of the seed.

It is evident from these associations that oil and protein do not vary in an exact inverse association as influenced by geographic source of the seed. The degree with which the seed is filled by the kernel is responsible, for the most part, in conditioning the differences in reserve capacity (Table 33). Since capacity and ratio are both most adequate in seed from the irrigated West,[2, 3, 68] this region must be considered the most favorable source of cottonseed of high mill-product value (considering only yields of oil and cake per ton of seed). Next in favor should be the Southeast, then the Mid-South (these last two produce seed of nearly equal average value), with the nonirrigated southwestern area providing seed of least probable value to the mills. In the irrigated region the ample supply of soil moisture and rather high even temperatures throughout growth allow ample opportunity for maximum development of kernels and deposition of oil and protein in the kernel. The varieties grown in this region are predominantly Acala and strains of American-Egyptian cottons that are perhaps above average in oil content.[3] Conditions for growth in the southeastern and mid-south regions may be equally as favorable as in the irrigated region but are not consistently so. Variability as to environment in specific seasons and localities contributes to a lower average in nonirrigated than in irrigated areas. Varieties used through the Mid-South and Southeast are quite numerous and the shift to new strains is continuous. A great many of those adopted recently [3] are relatively high in oil-to-protein ratio as well as in percentage reserve capacity; this may contribute to some extent to the relatively high quantitative composition of seed from these two regions. Some of the varieties used extensively in Texas and Oklahoma have a tendency toward high fuzz content and a resultant lowered percentage seed capacity. The continued occurrence of a near-drought condition in this area, however, is more logically responsible for seed that are often but poorly filled. The low oil-to-protein ratio of southwestern seed is related to the effects of limited soil moisture (and the accompanying limitation of nutrient uptake) on the pattern of development of the two reserve products. Protein is deposited continuously during boll maturation and thus has a greater comparative opportunity for reaching a high level under unfavorable conditions than has oil, which develops rapidly only at a critical period starting about twenty-five days after flowering.

Rainfall during May, June, and July was found [76] to condition the quantity of available oil in Arkansas cottonseed, 1910 to 1917, with a high oil content following high precipitation during these months with striking regularity. The few exceptions found were to be expected. Under

[76] E. R. Barrow and G. W. Agee, *Cotton Oil Press*, **2**, 44–45 (1918).

TABLE 33

Variation in Composition of Cottonseed According to Geographic Source[a]

Source of cottonseed	Source of data and years											
	Cresswell and Bidwell[b] 1914–15 to 1917–18				Pope *et al.*[c] 1935, 1936, 1937				Tharp *et al.*[d] 1942, 1943, 1944			
	Oil per ton, lb.	Cake per ton, lb.	Oil-to-protein ratio	Capacity[e]	Oil, %[f]	Protein, %	Oil-to-protein ratio	Capacity[e]	Oil, %[g]	Protein, %	Oil-to-protein ratio	Capacity[e]
Western irrigated region[h]	337	1112	0.989	41.19	—	—	—	—	18.35	19.76	0.928	38.11
Southwest[i]	285	885	0.889	36.54	20.24	24.37	0.831	44.61	18.11	19.19	0.944	37.30
Northern tier[j]	320	963	1.023	37.27	—	—	—	—	—	—	—	—
Mid-South[k]	309	1006	0.956	37.54	23.22	22.92	1.014	46.14	17.88	19.70	0.908	37.58
Southeast[l]	324	956	1.034	37.31	22.63	22.61	1.001	45.24	18.12	19.60	0.924	37.72

[a] Averages for each region and values for ratio and capacity calculated by the author.
[b] C. F. Cresswell and B. L. Bidwell, *U.S. Dept. Agr. Tech. Bull.*, **948** (1921).
[c] O. A. Pope and J. O. Ware, *U.S. Dept. Agr. Tech. Bull.*, **903** (1945).
[d] *Unpublished data.*
[e] Sum of the percentages of oil and protein.
[f] Based on moisture-free, acid-delinted seed.
[g] Based on fuzzy seed at 10% moisture content.
[h] California, Arizona, New Mexico, and irrigated valleys in Texas.
[i] Texas and Oklahoma and sometimes western Arkansas.
[j] Missouri, Kentucky, and Virginia.
[k] Arkansas, Mississippi, western Tennessee, and Louisiana.
[l] Eastern Tennessee, North Carolina, South Carolina, Georgia, Alabama, and Florida.

conditions prevailing in Texas, 1914 to 1917, high precipitation in May and June was associated with high oil content.[77] July rains were not directly associated with oil content but lack of rain in June—even with a wet May—occasioned a reduced oil content. As the protein content increases when the oil content decreases,[77] a high protein content can be expected (in Texas) after a dry May or June. In certain experiments conducted in Louisiana [76] and Arizona [79] reduced irrigation was associated with a small, poorly filled seed, which contained lower percentages of oil than seed produced under normal irrigation (or rainfall). Excessive irrigation seems to have no appreciable effect on cottonseed composition.[78, 79] In Tennessee high rainfall was found associated with a high oil and low protein content of cottonseed.[63] With one location omitted, these same data indicated low temperatures as being also associated with high oil and low protein content of the seed.

Atmospheric conditions are undoubtedly to some degree associated with variable composition in cottonseed. Certain relationships have been shown [72–75] but these are rather difficult sources of change to correlate exactly with performance. Very adequate composition is found for seed from western irrigated areas produced under conditions of low humidity and also from the Mississippi Delta area where high humidity prevails. Temperature may also be quite varied without showing an exactly correlated influence on seed composition—Shafter, California, has higher temperatures on the average than State College, New Mexico,[79] while both regions often produce seed of very high oil and protein content. Soil type and comparative fertility are of considerable importance in relation to composition of seed (see Section V) but these factors vary considerably within each large geographic area.

B. Qualitative Composition

Jamieson and Baughman [69] studied the quality of oils in the United States Cotton Belt by analysis of seed and oils furnished from mills in the Southwest and Southeast. They found but little variation associated with geographic source, and concluded that, with few exceptions, the refractive index, the specific gravity, and the saponification value are practically constant. Iodine numbers of the majority of samples varied between 106 and 109 and the percentages of unsaturated acids agreed within less than 2%. Morrison and Bosart [70] restratified these data to find that oils from north of latitude 34° were slightly higher in iodine value and refractive index and lower in titer and saturated fatty acids than oils from south of latitude 33°. These differences were small and

[77] J. Malowan, *Cotton Oil Press*, **4**, 51–52 (1920).
[78] W. H. Tharp and H. B. Brown, *unpublished data.*
[79] W. H. Tharp, *unpublished data.*

mostly within the limits of what had been considered relatively constant composition by Jamieson and Baughman. From results of their own analyses Morrison and Bosart concluded that seed from the northwest section (most of Arkansas and Oklahoma and a part of Texas) should give oils with the lowest amount of stearin. Jamieson and Baughman had concluded that refining may exert as much influence on the composition of refined cottonseed oil as variations in soil, climate, and latitude. Meloy [72–75] has shown that there is considerable variation in the free fatty acid content of cottonseed oils according to location; he attributed the variations to differences in aerial environment during opening of the boll and after-ripening of the seed rather than to the status of nutrient or moisture supply in the soil. The conditions suggested, as conducive to the development of high free fatty acid content were hot and humid weather. These conditions are part of the influence of geographic source, but only in a limited manner, so that wide differences as to free acids often occur in lots of seed grown relatively few miles apart.[75] Such variations are strictly seasonal and are mostly location-year influences rather than an integral part of large geographic source differentials.

V. Relative Maturity

Cottonseed are mature in reference to composition only when no further changes in depositions or growth occur with continued after-ripening; with the time necessary for maturity of composition being dependent on the variety and all the environmental stresses that might advance or delay the process. Because of the indeterminate mode of fruiting in cotton, bolls are usually found at several stages of maturity at any one picking. Even bolls that are fully open and similar in appearance can be different as to time of opening and may thus differ with respect to the composition of the seed.

The average trend is found to be an increase in oil content from early to late pickings in experimental plots, [5, 20, 43, 79] and an increase in the oil content of samples received at the mill with advance in season during the first three to four months of the harvest period.[39, 68, 73, 80, 81] Change in protein with advance in season is less marked and best characterized as a slight increase, although many exceptions are found.[68, 73] The total percentage reserve capacity, at least, tends toward an increase with lateness of harvest. Often the later harvested seed are heavier,[5, 79, 82] have a higher percentage kernel content,[5, 79] and have a higher content of oil, if not of protein, in the kernels.[79] These are the trends. The higher kernel

[80] O. F. Joseph, F. G. Martin, B. W. Whitfield, and J. S. Hancock, *Welcome Trop. Res. Labs. Chem. Pub.*, **26,** 12–30 (1923).

[81] G. S. Meloy, *Oil & Soap,* **16,** 174–178 (1939).

[82] F. M. Eaton, E. W. Lyle, J. T. Rouse, G. W. Pfeifenberger, and W. H. Tharp, *J. Am. Soc. Agron.*, **38,** 1018–1033 (1946).

and the higher oil and protein content of the seed undoubtedly represents a more mature condition. There are more immature bolls harvested in the early pickings than at the latest harvest when all remaining bolls have been open for a long period and thus are completely after-ripened. Reference to Section I of this chapter will reveal that a great many of the changes in structure and composition of the seed are not complete until some time after the bolls open. Oil, it is true, develops rapidly at a period just before the boll is open, but it continues to increase slowly well beyond this critical period. Protein is usually found to increase slowly until a constant composition of the seed is attained. This view, in regard to immaturity of early seed, is more accepted than proved but it is at least reasonable. The other associated, and not exactly tested influence, is that of weather. The later-formed bolls are matured in cooler weather (August through December) and usually in a more humid atmosphere. These conditions associated with lateness delay drying out of the open bolls and undoubtedly contribute to increased deposition through maintenance of translocation to the seed. At least this has been found essentially true with soybeans [83] and flax seed.[84]

Meloy [73, 74, 81] and others [68, 79] have noted certain exceptions to this trend. Drought, defoliation, and early frost have been cited [74] as reasons for continued reduction from November on, in both oil and protein content of seed from certain Texas counties in the 1942–43 harvest. A similar reduction in oil content was noted in Mississippi seed in the 1937–38 harvest, but here the weather was hot and humid in early fall, and deterioration of the seed (evidenced by high moisture content of the seed and free fatty acid in the oils) was an associated factor.[73, 81] Exceptions to the trend toward increase in oil with advance in season were also recorded in other states and other years.[73] Botkin [43] noted irregular increases in the percentages of oil and protein in seed with advance in season in New Mexico. Many such deviations as to specific location-year are recorded in the compilations by Cresswell and Bidwell,[68] although the average was a slight increase in oil content up to December. For two successive years flowers were tagged and dated in an experiment [78] carried out in Louisiana. Analyses of seed from these dated bolls showed a reduction in size of seed and percentages of oil and protein in both years, but high fertilization tended to give later-initiated seed an equal or improved oil and protein content. The top crop from an experiment [85] in Georgia tended also to have seed of higher oil and protein content than the early bottom crop where adequate potash was supplied the plants, but without fertilization these same plants produced less oil in the late seed, and the specific trends were found

[83] J. L. Cartter and T. H. Hopper, *U.S. Dept. Agr. Tech. Bull.*, **787** (1942).
[84] A. C. Dillman and T. H. Hopper, *U.S. Dept., Agr. Tech. Bull.*, **844** (1943).
[85] W. H. Tharp and J. H. Turner, *unpublished data.*

TABLE 34. Summary of Effects of Nitrogen, Phosphorus, and Potassium on Production and Composition of Cottonseed

Element of nutrient supply increased	Product measured	Effects of increase in level of supply of nitrogen, phosphorus, and potassium found by previous investigators as listed					
		Garner *et al.*[a]	White[b]	O'Kelly *et al.*[c]	Gieger[d]	Seale[e]	Wadleigh[f]
Nitrogen	Yield of seed cotton	Increased	—	(Nitrogen + phosphates) Increased	Increased	Increased	Increased
	Per cent lint	Decreased	—	No sig. effect	—	—	Decreased
	Seed weight	Increased	Increased	Decreased	—	—	Increased
	Per cent kernels	Increased	Increased	—	—	—	—
	Per cent oil in seed	Decreased	Increased	Decreased	Decreased	Decreased	Decreased
	Per cent nitrogen in seed	—	—	Increased	Increased	—	Increased
Phosphorus	Yield of seed cotton	Decreased	—		Slight increase	Little effect	
	Per cent lint	Increased	—		—		
	Seed weight	No effect	Increased		—		
	Per cent kernels	Increased	Increased		Little effect	Little effect	
	Per cent oil in seed	No effect	Increased		Slight increase	—	
	Per cent nitrogen in seed	—	—				
Potassium	Yield of seed cotton	Increased	—	Increased	Slight increase	Little effect	
	Per cent lint	No effect		Little effect		—	
	Seed weight	Increased	Increased	Increased		—	
	Per cent kernels	No effect	Slight increase	—		—	
	Per cent oil in seed	Increased	Slight increase	Increased	Little effect	Slight increase	
	Per cent nitrogen in seed	—		Decreased	Little effect	—	

[a] W. W. Garner, H. A. Allard, and C. O. Foubert, *J. Agr. Research*, **3**, 227–249 (1914). Used variations in level of each element in complete fertilizers, on a "very poor" soil, Manning, S. C., 1911. Upland cotton.

[b] H. C. White, *Georgia Expt. Sta. Bull.*, **114**, 237–268 (1915). Used variations in level of each element (including zero concentrations) in complete fertilizers, Experiment Station, Ga., 1911–1912.

[c] J. F. O'Kelly, W. W. Hull, and M. Gieger, *Mississippi Agr. Exp. Sta. Tech. Bull.*, **20** (1933). Used five levels of potash in complete fertilizer; nitrogen plus phosphate compared to no fertilizer; three locations in Miss., 1926–1931. Upland cotton.

[d] M. Gieger, *J. Agr. Research*, **63**, 49–54 (1941). Used variations in single elements on Yazoo-Mississippi Delta soils, Stoneville, Miss., 1933–1937. Upland cotton.

[e] C. C. Seale, *Trop. Agr. Trinidad*, **29**, 210–214 (1942). Used N, P, and K fertilizers in a two-level factorial experiment, St. Vincent, B.W.I., 1938–1939. Two strains of Sea Island cotton.

[f] C. H. Wadleigh, *Arkansas Agr. Expt. Sta. Bull.*, **446** (1944). Used four levels of nitrogen supply in greenhouse, sand nutrient culture, Fayetteville, Ark., 1936. Rowden 2088 upland cotton.

to differ from year to year. Under greenhouse conditions early- and late-formed bolls were found [20] to differ little in average oil content. When nitrogen nutrition was low, however, increase in protein and decrease in oil occurred with advance in the season, whereas the reverse (decrease in oil and increase in protein) held true when an adequate supply of nitrogen was given the plants. Diseases that kill plants or seriously limit translocation during boll maturation may cause more immature seed to be found in the later harvest and thus induce a lowered oil and protein content.[79, 82]

The trend toward more oil in later-initiated seed results from a series of interrelated influences and stresses. Certainly not the least of these is the earliness potentials of the varieties, which vary widely. The specific result obtained in the field would depend upon the variety under study. Varieties also differ widely as to retention of bolls under stress, and the ensuing differences in boll load could have a marked effect on composition of early- as compared to late-set bolls, particularly if a marked stress such as drought occurred only after early bolls had become fully mature.

VI. Nutrition

The effects on cottonseed composition of increase in most elements of nutrient supply are related to the comparative availability and balance of the nutrient complex. Exact dependent factors that influence composition can be worked out accurately only in controlled greenhouse studies, where each phase of the environment is subject to measurement and regulation. One such study has been reported,[20] but most of the available information concerning the influence of nutrition on cottonseed composition has been obtained from field experiments.

Prior to 1945 there had appeared but few reports [5, 8, 20, 35, 64, 86] concerned specifically with the effects of variation in the level of nutrient supply on composition of cottonseed; these are summarized in Table 34. More recently, an extensive study has been made possible through the collaboration of investigators carrying out the cooperative Federal-States cotton improvement program.[87]

Early reports (Table 34) of the influence of nitrogen-phosphorus-potassium fertilization on the composition of cottonseed are not in entire

[86] J. F. O'Kelly, W. W. Hull, and M. Gieger, *Mississippi Agr. Expt. Sta. Tech. Bull.*, **20** (1933).

[87] Seed were analyzed from 22 different cotton fertilizer trials, some of which were carried at several locations and for more than one year. Studies were included from different geographic areas and a wide selection of varieties (American upland and Sea Island) were tested. Although not all of these studies were complete with regard to the use of all three main elements—nitrogen, phosphorus, and potassium—there was sufficient repetitional information to allow establishment of probable trends in composition of cottonseed as influenced by the level of single elements of supply. The results of these experiments are to be reported in a series of U.S. Department of Agriculture Technical Bulletins.

agreement. The data were presented on different bases of measurement, occasioning some disparity as to results, but disagreement lay in interpretation of the specific results obtained rather than in finding differences in principles involved. Soil types, climates, and particularly the residual availability of the nutrients varied from one test area to the next. Exact differences among both early and later reports are developed under the specific subheads that follow.

A. Nitrogen Supply

Increase in the level of nitrogen supply has been found associated with an increased protein content of cottonseed (see Fig. 18), with but one

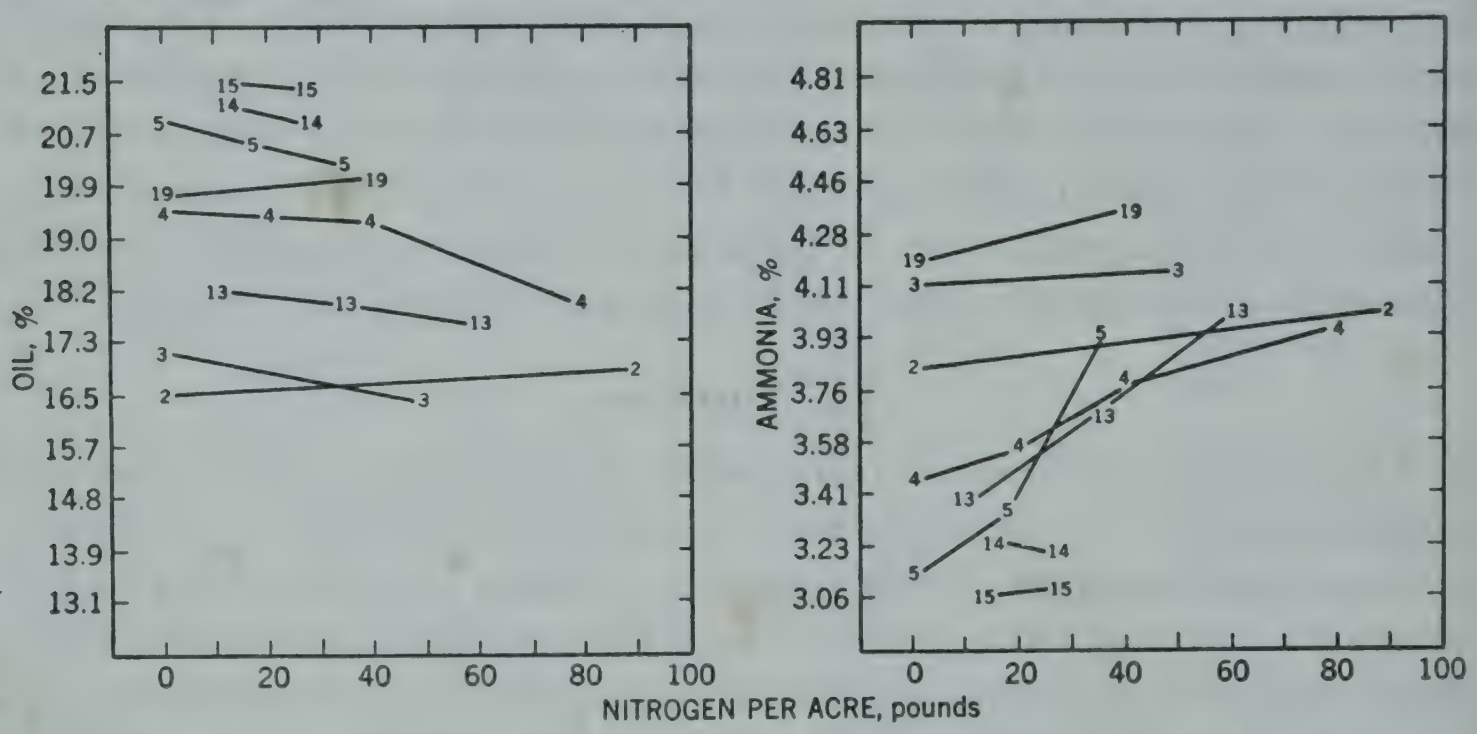


Fig. 18. Changes in oil and ammonia content of cottonseed associated with increase in nitrogen supply.[79] Numbers on curves refer to the different experiments.

exception.[79] Conversely, an increase in the available supply of nitrogen has been associated rather consistently with a decrease in the percentage of oil in kernels and seed. Slight increases in oil content were observed in three studies,[8, 78, 79] but the general trend was for the increase in protein to be greater than the decrease in oil content. This resulted in lowered oil-to-protein ratios and higher percentage reserve capacities of kernels and seed. Seed were found to be heavier and to contain higher percentages of kernels in most studies. The production of smaller seed accompanied nitrogen plus phosphate applications in one study,[86] but the use of large amounts of nitrogen usually increased seed size and the percentage of kernels. Nitrogen fertilization tends to decrease the fuzz content of cottonseed, but the result seems to vary with the experiment and is probably less directly associated with nitrogen nutrition than are other compositional variations in cottonseed. Increase in nitrogen supply tends to increase the number of seed per boll,[78] and in the majority of cases the

changes in seed composition are associated with increased yields of seed cotton, with a tendency [5, 20, 86] toward decreased gin out-turn (per cent lint). All of these factors combine to produce higher yields per acre of oil and cake but a slightly decreased grade of cottonseed as the level of nitrogen supply to the plant is increased.

B. Phosphorus Supply

Increase in the supply of phosphorus to cotton plants may occasion significant variations or result in little or no change in the percentage composition of the seed. The result obtained with phosphorus seems often to be more related to the manner in which it influences the comparative availability of nitrogen or potassium than to a direct effect of phosphorus supply. Its increase has occasioned increased per cent oil content of seed,[8, 64, 78] decreased oil content,[79, 88] and increases followed by decreases

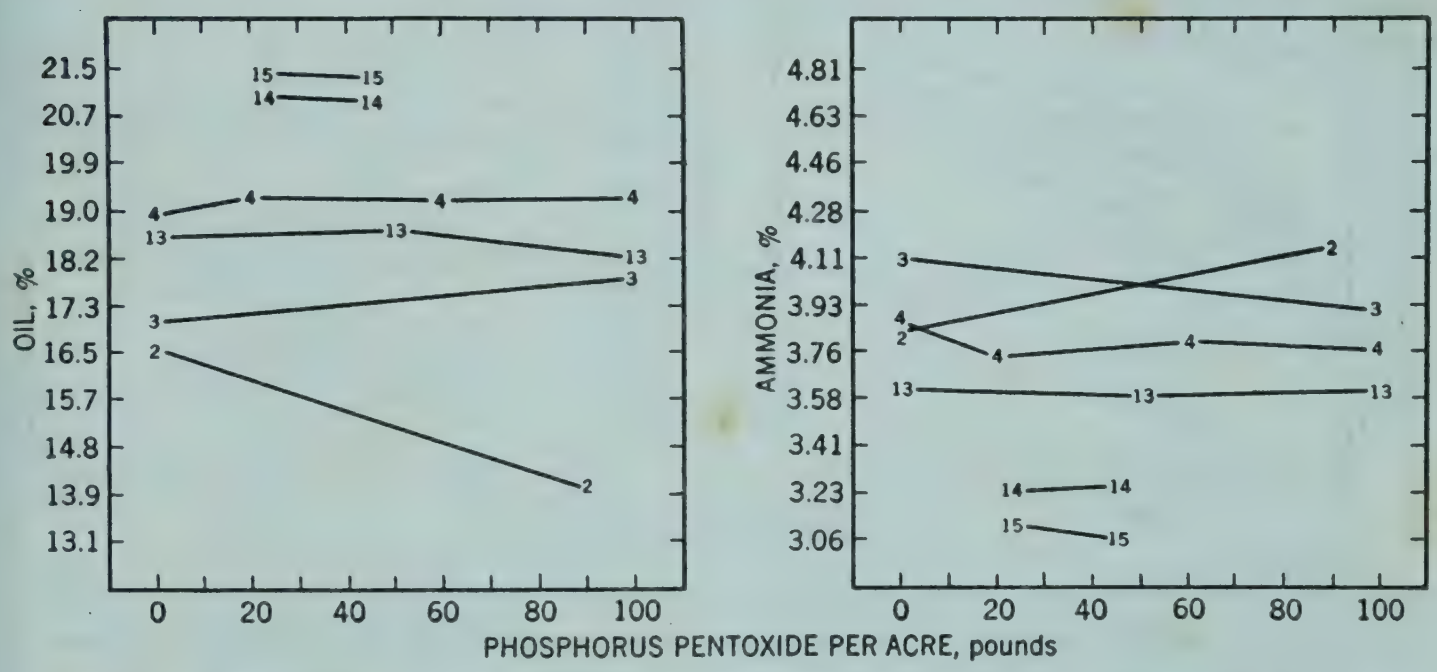


Fig. 19. Changes in oil and ammonia content of cottonseed associated with increase in phosphorus supply.[79] Numbers on curves refer to the different experiments.

with increasing rates of application [73] (see Fig. 19). The trend of effect on protein is the inverse of that for oil content, the protein increasing or decreasing as the oil is decreased or increased, respectively. This close inverse variability for oil and protein results in little change of percentage reserve capacity, but produces marked variations in the oil-to-protein ratio in the kernels and in the seed. There may be slight increases [5, 8] in weight and per cent kernels in the seed, although significant decreases in these two measures have been noted also.[88] A high phosphorus supply tends to reduce the per cent of fuzz on cottonseed without lowering the seed weight [78, 88] with the per cent of kernels in the same seed being unaltered [78] or decreased. Per cent lint in seed cotton, however, may be increased significantly by phosphorus fertilization. There seems to be no

[88] W. H. Tharp, J. J. Skinner, and R. P. Bledsoe, *unpublished data.*

adequate basis for systematic deductions in regard to the trend of variability in composition of cottonseed as influenced by phosphorus supply. The use of phosphorus will be found generally beneficial to acre yields of oil and cake only where the yields of seed cotton are found to be increased sufficiently to guarantee a greater yield of seed, regardless of its partial composition.

C. Potassium Supply

Increase in the level of potassium supply increases the oil content of cottonseed in nearly all instances (Fig. 20). Several cases have been reported where only a slight increase, or little effect, was observed,[8, 35, 64, 79] and in still others a second increment of potassium failed to give the benefit

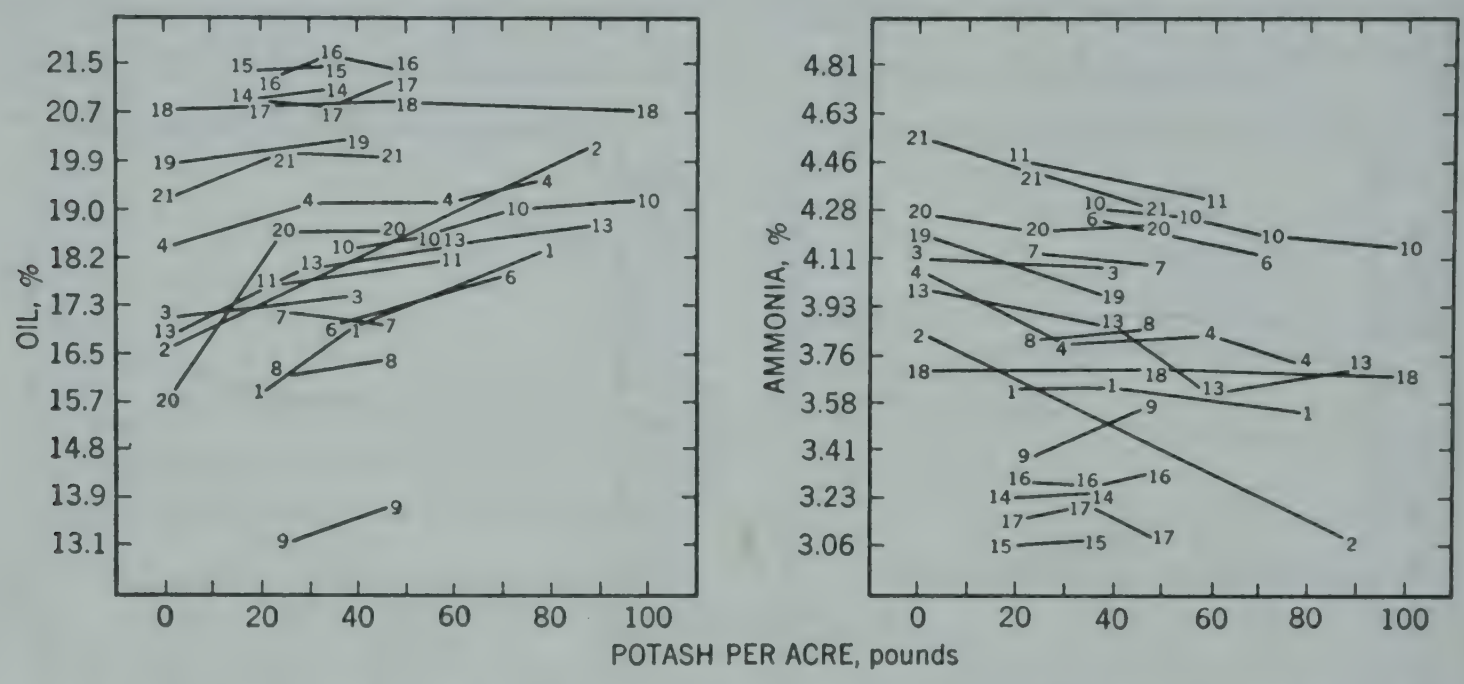


Fig. 20. Changes in oil and ammonia content of cottonseed associated with increase in potassium supply.[79] Numbers on curves refer to the different experiments.

in increased oil content of seed obtained with the initial application.[79] Garner *et al.*[5] reported no effect with potash, but restratification[85] of their results, as regard to increased potash supply, shows a marked increase in oil content of the kernels. An increased potassium supply results in a reduction of the protein content of cottonseed, with the average reduction being of lesser degree than the increase in oil content. This tends to produce a higher oil-to-protein ratio and an increased percentage reserve capacity of seed and kernels with an increased level of potassium in the nutrient supply. In several cases percentages of both oil and protein were increased simultaneously, and in only one study were percentages of both reserves reduced by potash fertilization.[79] Seed weight and percentages of kernels tend to be increased by potash fertilization. Although such increases may be small, there are no reports of significant reduction in these two measures with an increased supply of potassium. The fuzz content of seed may likewise be increased,[88] although it may be practically unaltered at the

same time that other significant changes are induced in the same seed.[78, 79, 85] As a result of increased ratio and capacity the grade of cottonseed will tend to be increased by potash fertilization, and increased yields of both oil and cake per ton of seed will result. Where increased yields of seed cotton are also obtained, the applications of potash fertilizers will markedly increase the acre value of the seed.[79]

D. Interactions

There are undoubtedly certain interactive influences of nitrogen, phosphorus, and potash supply on cottonseed composition. The exact trends occasioned by such influences might be established by means of pure-culture, greenhouse studies, but the interrelated effects on one measure of composition would be expected to be different and not exactly related to interactive influences on another measure. Field studies show that this is the case since percentage reserve capacity of kernels, for example, is altered by the various rates and ratios in a manner different from the

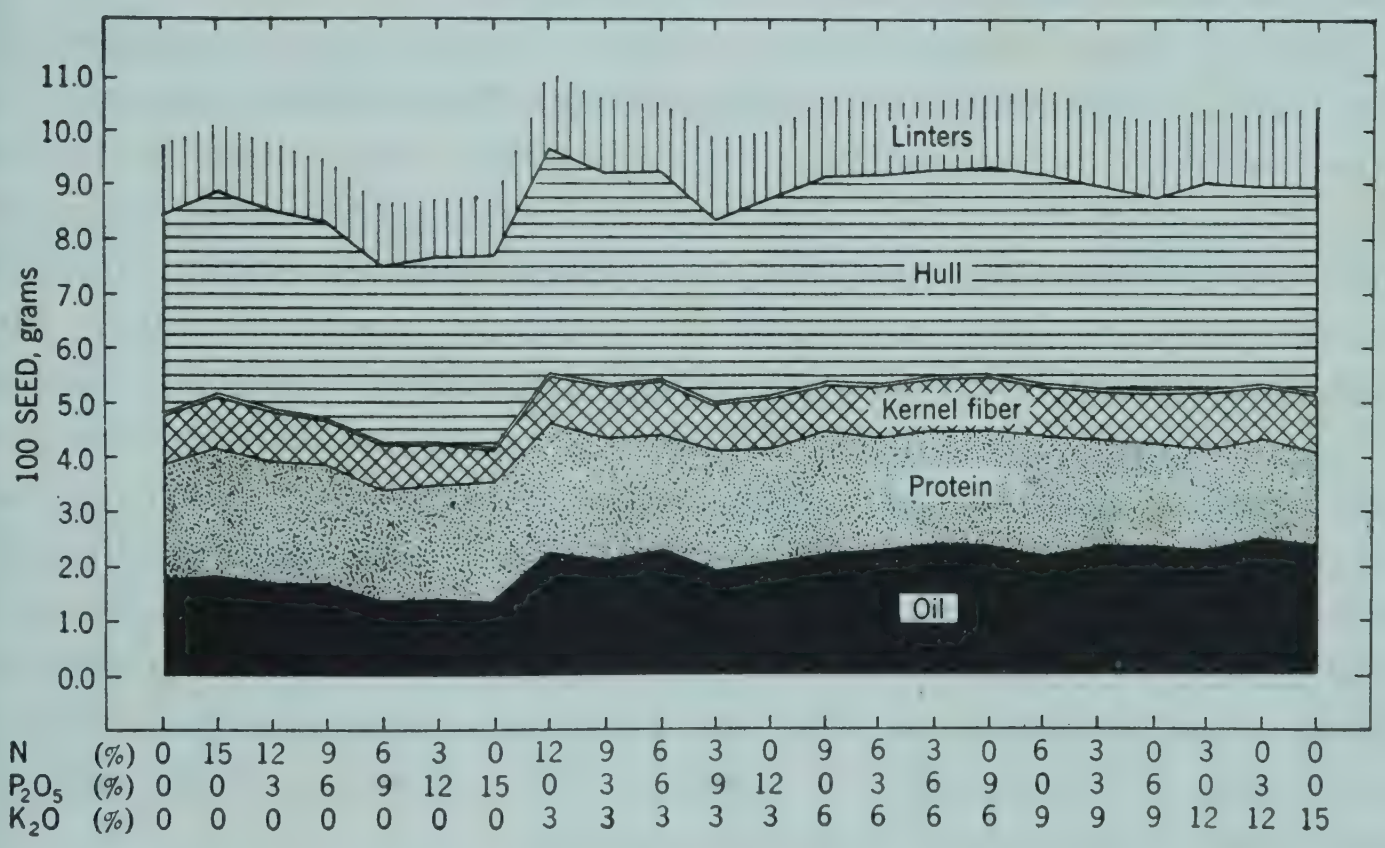


Fig. 21. Variations in weight and partial composition of cottonseed as influenced by ratio of nitrogen, phosphorus, and potassium fertilization; fifteen parts total plant food applied at the rate of 500 pounds per acre.[88]

percentages of oil, of protein, or of fuzz and kernel in the seed (Fig. 21). Field studies do not allow for any determination of probable trends because the exact result in any instance is always dependent upon the residual supply of nutrients as well as the applications of fertilizer. Deductions from the particular to the general would be extremely hazardous. Other phases of the environment[78, 79] have considerable effect on the manner in which the composition of seed is altered by simultaneous

variation of two or more constituents of the nutrient supply. Indeed, the exact effect of increase in any of the three principle components of the nutrient supply is so affected by the other phases of environment, and by varietal potentials, that generalities may be stated only because considerable repetitional information is available for the basis of such conclusions.[79]

E. Other Elements

The *sodium* level tends to affect cottonseed composition in the same manner as the potash level, but data are limited and the proof relatively inconclusive.[79]

Calcium when applied as lime,[79, 88] as gypsum,[79] or as neutral calcite [79] does not appear to alter the composition of seed because of increase in calcium *per se*. The variations more probably result from alterations of soil *p*H and the accompanying changes in availability of other plant foods.

Magnesium supply has been studied very little,[79] and no significant effects on cottonseed composition are reported.

Each of these three elements: sodium, calcium, and magnesium has been tested insufficiently to establish trends. The available evidence indicates that they are not limiting in regard to seed composition in the same sense as has been found for variations in nitrogen, phosphorus, and potassium, but this does not preclude any dependencies on certain minimum amounts that are found necessary for optimum growth of cotton. Data concerning influence on seed composition of the other "essential" elements of the nutrient supply: sulphur and iron are entirely lacking. Certain so called "minor elements" of supply have a definite effect on growth and undoubtedly condition relative composition of seed, but usually only where concentrations are below minimum requirements or in excess of plant tolerances. Such limitations are an important consideration of fundamental aspects of nutrition. They are, however, seldom encountered where good yields of cotton may be obtained with additions of the ordinary commercial fertilizers and natural manures.

VII. Production and Composition

An intimate relationship between the production of seed and variation in composition does not exist among varieties of cotton.[3] Such a relationship may result among variations induced by changes in environment in some instances,[79, 85] but the associated variations in yield and composition differ considerably from one test to the next.[79] An increased yield may accrue entirely through an increase in seed size, but more often it will occur through an increased number of bolls per acre, regardless of the composition of the seed. The total value of (prime) seed to the producer

(if sold on a grade basis) is derived from both yields of seed and the percentage reserve composition.

An increase in 10 points grade value of prime seed [89] from approximate one bale per-acre yields (900 pounds of seed) would net the producer $2.52 at current seed prices ($56.00 per ton). This could result from a 2.5% greater oil content or a 1.67% greater ammonia content of the seed, yet this same increase in the acre value of seed could be accomplished by an increased yield of 90 pounds of seed (basis grade). The chance of having 90 pounds average difference in seed yield is greater than that of finding 2.5% more oil or 1.67% more ammonia in the seed. Thomas and Gerdes [49] report that about $5.00 per ton of seed corresponded to the average greatest differences in composition among 12 varieties tested at 6 locations on Mississippi Delta soils in 1944, and about $2.00 per ton of seed represented the greatest difference among locations. Greatest within-test differences among varieties in the Regional Spinning Study [3] in 1943 ranged from but a few points to 20 points grade, although not among the same varieties. Where the same varieties were compared at different locations (Table 35) considerable disparity was in evidence as to performance in terms of both grade and yield of seed.

TABLE 35

Associated Differences in Yield and Grade of Seed for Two Varieties of Cotton at Seven Locations, 1943[a]

Location[b]	Stoneville 2B		Deltapine 14	
	Yield, pounds	Grade, points	Yield, pounds	Grade, points
State College, New Mexico	2002	106.6	2392	110.9
Sacaton, Arizona	1412	103.3	1263	100.6
St. Joseph, Louisiana	1775	105.2	1577	102.6
Stoneville, Mississippi	1305	101.7	1200	95.7
State College, Mississippi	959	97.1	836	92.2
Chillicothe, Texas	687	107.5	617	100.7
College Station, Texas	262	89.1	238	92.7

[a] W. H. Tharp, *unpublished data.*

[b] Locations chosen as examples. Yields and grades are not necessarily representative.

In certain fertilizer studies [79] the greatest induced differences in average grade and the associated alterations in acre yield (Table 36) indicate that increases in yields of seed through fertilization are often accompanied by significant increases in the grade value of the seed.[78, 79, 85, 88] The magnitude of change in either grade or yield, however, bears no relation-

[89] This discussion is presented in full recognition of the importance of the differential in price for lint cotton as compared to that for cottonseed. The acre value of lint has received ample consideration, while seed value usually is either neglected or considered at basis grade only.

ship to the magnitude of change in the other component of total acre value of seed as induced by change in level of nutrient supply.

In consideration of any selection among varieties there may be considerable reason for choosing a variety or strain with a characteristically high grade-value seed in the face of some slight loss in acre production of seed, providing the acre value of lint was not thereby reduced. Where differences are induced, as with fertilization, the more obvious increase in yield of seed seems to be the best criterion of choice, since a higher grade quite often accompanies significant increases in acre yields of cottonseed.[79]

TABLE 36

Greatest Within-Test Differences in Yield of Seed and Associated Change in Cottonseed Grade with Different Fertilization Treatments[a]

Fertilizer experiment	Treatment producing		Increased yield of seed, pounds	Change in grade, points
	Lowest yield	Highest yield		
Tharp and Turner[b]	20 lb. K_2O	80 lb. K_2O	201	+11.0
Tharp and Brown[c]	50 lb. N	100 lb. P_2O_5, 40 lb. K_2O, 20 tons manure	639	+ 4.0
Tharp *et al.*[d]	500 lb. of 0-15-0	500 lb. of 6-6-3	497	+21.3
Tharp,[e] Test no. 4[f]	Nothing	100 lb. of 4-8-3	439	+ 4.6
Tharp,[e] Test no. 5	Nothing	36 lb. NO_3	524	+ 1.7
Tharp,[e] Test no. 7	24 lb. K_2O	48 lb. K_2O	185	− 2.7
Tharp,[e] Test no. 9	24 lb. K_2O	48 lb. K_2O	30	+ 5.6
Tharp,[e] Test no. 10	36 lb. K_2O	144 lb. K_2O	99	+ 4.4
Tharp,[e] Test no. 13	No phosphate 35 lb. N, 60 lb. K_2O	100 lb. P_2O_5, 35 lb. N, 60 lb. K_2O	192	+ 1.4

[a] Figures for fertilization treatments and yields are on a per-acre basis.
[b] W. H. Tharp and J. H. Turner, *unpublished data.*
[c] W. H. Tharp and H. B. Brown, *unpublished data.*
[d] W. H. Tharp, J. J. Skinner, and R. P. Bledsoe, *unpublished data.*
[e] W. H. Tharp, *unpublished data.*
[f] Test numbers refer to same numbers in Figures 18, 19, and 20.

CHAPTER V

BIOLOGICAL PROCESSES OF THE COTTONSEED

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"If we want to elucidate some fundamental biological principle, it does not matter whether we study a high or low animal, a plant, or the yeast cell. There is no fundamental difference between kings and cabbages."
Albert v. Szent-Györgyi [1]

I. Introduction

The cotton and cottonseed oil industries annually sustain substantial losses as a result of the biological activity in the cottonseed. That portion of the cottonseed crop which is reserved for replanting must be protected from loss in viability and vigor until the following planting season. In many localities the atmospheric temperature and humidity are such that biological activity in the seeds is too high for safe storage. These conditions result in a high mortality in the stored seeds and the consequent losses contribute increased costs of cotton production.

The biological changes which take place in the surplus seeds intended for food and industrial uses are of equal importance. The cottonseed oil and feed industries are dependent for successful operation upon obtaining high yields and products of good quality from their raw material. Excessive biological activity in the seeds, either in the field prior to harvesting or subsequently during storage, will result in a reduction both in the quality and the yield of oil and meal. Extensive deterioration of cottonseed which occurs annually in many localities and periodically in most regions where cotton is grown may make the difference between profitable and unprofitable operation of an oil mill. Profitable operation of the crude oil mill is, of course, reflected in more profits for the producer, ginner, and refiner. The economic consequences of biological activity in cottonseed are, therefore, of sufficient importance to justify every reason-

[1] A. v. Szent-Györgyi, *Studies in Biological Oxidation and Some of Its Catalysts*, Barth, Leipzig, 1937; Stechert, New York, p. 67.

able effort to understand this activity and if possible to control it by chemical or mechanical means.

II. General Properties of Viable Seeds

Living material utilizes its resources of potential energy for the purposes of growth and reproduction. The manner in which the energy is utilized differs in detail in the various forms of life, and as the plant or animal becomes more complex, more controls are developed to regulate and integrate the activity within its tissues. Fundamentally, all life processes apparently follow simple thermodynamic principles which hold regardless of the type of organ or material involved. An understanding of the biological processes of the cottonseed, therefore, must be based on those fundamentals which are common to all types of living matter and from these one can proceed to the special details which are peculiar to this species of seed.

Certain properties of seeds become self-evident when it is considered that seeds exist for the purposes of propagating their species and must, therefore, contain all the essentials for initial development and growth. They must contain certain types of food reserves which in the case of cottonseed are primarily fat and protein and to a lesser extent carbohydrate which is available as a quick source of energy. The purpose of these reserves is two-fold: (*a*) they serve as a source of raw materials from which the new cellular constituents are synthesized during germination, and (*b*) they provide a source of the energy required to support the synthetic processes. The investigations on the *in vitro* synthesis of glycogen and starch by Cori [2] and Hanes [3] have provided ample proof that only through the production of intermediate organic phosphate compounds, which contain considerable energy in the phosphate linkage,[4] can complex carbohydrates be formed from simple sugars.

In addition to the food reserves which seeds must contain, viable seeds must be provided with the full complement of enzymes or enzyme precursors required to carry out the processes of growth. Enzymes are the biological catalysts which make possible the wide range of chemical processes constantly occurring in living matter. They are proteins, either simple or conjugated, are generally thermolabile, and are very specific in their action. Each enzyme will catalyze one specific reaction or a limited group of reactions and will react only with a restricted number of substrates. Thus phosphorylase, which catalyzes the synthesis of glycogen from hexose-1-phosphate, will not react with hexose-6-phosphate,[2] and lactic acid dehydrogenase (catalyzing the reaction, lactic

[2] C. F. Cori and G. T. Cori, *Ann. Rev. Biochem.* **10,** 151–180 (1941).
[3] C. S. Hanes, *Proc. Roy. Soc. London*, **B128,** 421–450 (1940).
[4] F. Lipmann, in *Advances in Enzymology,* Vol. I, Interscience, New York, 1941, pp. 99–162.

acid ⇄ pyruvic acid) will react with *l*-lactic acid and not with its optical isomer.[5] Any treatment which will denature proteins may inactivate enzymes. They are inactivated by heat, oxidation, surface denaturation, extremes of acidity or alkalinity, or hydrolysis. Enzymes generally are active within definite regions of *p*H (*e.g.*, pepsin requires an acid medium; and trypsin, a slightly alkaline medium for optimum activity), and they can be inhibited by specific poisons. It has been possible to prepare many enzymes in a highly purified state, and in some instances crystalline enzymes have been obtained.

When relatively pure preparations are used, the catalytic activity of enzymes follows well defined kinetic patterns, rate constants may be determined, and the mechanism of their mode of catalysis may be elucidated.[6] Even in tissue extracts, the kinetics of enzymatic activity may differ but little from that observed with the pure enzyme. Extraneous tissue material in an enzyme extract often exerts little or no influence upon the activity of the enzyme under investigation.

In intact tissue and in normally functioning living organisms, enzymes generally do not function as individual catalysts independent of their cellular environment, and various chemical and physical controls serve to limit and integrate the activities of the various types of enzymes. Let us consider a sequence of events occurring in germinating cottonseeds, for example, hydrolysis-oxidation-synthesis. There are enzymes which catalyze the hydrolysis of the glycerides and proteins in the cottonseed; there are other enzymes which catalyze the oxidation of a variety of substrates including some of the hydrolytic products; and there are still other enzymes which utilize the energy obtained from oxidation to synthesize new cellular material from the simple compounds obtained by hydrolysis. In normal intact tissue, these three processes are controlled and integrated but in an extract of seedlings, although both hydrolytic and oxidative activities are still present, they are no longer integrated and controlled. Each type of activity proceeds independently of the other and at a more rapid pace than in the intact seedling. Because of this lack of integration, the activities of the hydrolytic and oxidative enzymes are not coupled and no synthesis takes place in the extract.

The nature and extent of the biological processes which take place in seeds will, therefore, depend on that complex relationship between food reserves, enzymes, and the degree of integration and control which exists at any given moment.

III. Biochemical Methods

The extent of our knowledge of the biological processes in living matter is largely determined by the degree of refinement which has been attained

[5] F. Kubowitz and P. Ott, *Biochem. Z.*, **314,** 94–117 (1943).
[6] H. Lineweaver and D. Burk, *J. Am. Chem. Soc.*, **56,** 658–666 (1934).

in methods for the observation of biological activity. As we proceed from crude qualitative observations to precise quantitative measurements, it becomes increasingly possible to correlate and integrate individual observations and to formulate general laws of biological behavior. It must be emphasized that the only type of observation that ensures further progress is a quantitative one. The fact that a sample of cottonseed does or does not respire is of little value and consequence compared to a quantitative evaluation of the *rate* and *intensity* of respiration. The knowledge that one sample of seeds has developed more free fatty acids during storage than another is likewise of relatively little fundamental value. When, however, the same information can be stated in terms of a lipolysis *rate constant,* it becomes possible to utilize this information to unravel the complex mechanism of lipolysis.

Biological activity may be observed in intact organisms (*in vivo* observations) or in tissue sections, macerated tissue, or tissue extracts (*in vitro* observations). *In vitro* observations may be made under conditions where all of the reactants are present in pure form (salts, substrates, crystalline or highly purified enzyme preparations, etc.) without any trace of the presence of original tissue material. In general, both types of observations are necessary, and the ultimate goal of biochemical research is to enable us to explain *in vivo* observations in terms of reactions which have been discovered and investigated by means of *in vitro* techniques.

Observations of the respiration, heating, and lipolysis of intact cottonseed are examples of *in vivo* experiments. These observations may be placed on a quantitative basis and correlations established between the various types of activities. However, if all biological investigations were limited to observations of this type, it would be impossible to progress very far toward a complete understanding of the mechanism of these reactions. It, therefore, becomes necessary to determine the nature of the systems involved in the above processes by means of *in vitro* observations. Any biological oxidations require the intervention of oxidases, hydrolysis of proteins, the action of proteolytic enzymes, hydrolysis of glycerides, the action of lipases, etc.

If it is desired, for example, to determine whether lipases are present in cottonseed, it is only necessary to investigate the effect of the addition of ground cottonseed or cottonseed extracts on the rate of hydrolysis of a pure triglyceride or cottonseed oil. If activity is observed, *i.e.*, the rate of hydrolysis is increased by the presence of macerated tissue or tissue extract, it can be readily determined whether the catalyst is an enzyme by subjecting the catalytically active material to the usual tests for an enzyme, *e.g.*, tests for proteins, and for thermal lability, sensitivity to *p*H, specificity, etc.

In an attack upon any enzyme problem recourse must be taken to the

great amount of accumulated knowledge of enzymology. Even though there may be specific differences between enzymes from different types of living matter, it should be borne in mind that there are classes of enzymes which perform specific functions and that there is enough in common between the enzymes in each class to warrant the *a priori* assumption that methods which detect one enzyme will be successful in the case of other enzymes of the same class. Thus, if it is desired to determine whether there is a peroxidase in cottonseed (an enzyme which catalyzes the oxidation of organic substrates by hydrogen peroxide), it is only necessary to apply techniques which are successful on peroxidases from other sources to reach an evaluation relative to cottonseed tissue.

However, considerable care must be exercised in the interpretation and evaluation of *in vitro* observations. It does not necessarily follow that, because a certain type of enzymatic activity cannot be detected in tissue extracts, this activity is absent in the intact tissue. Many enzymes are very unstable and may be inactivated in the process of extracting them from their normal environment. Other enzymes are so firmly bound to contiguous cellular material that they cannot be readily extracted. Conditions of extraction which are suitable for the removal of a given enzyme from one type of tissue may be totally inapplicable to the same enzyme associated with a different type of tissue.

Conversely, if an enzyme is detected in a tissue extract, it does not necessarily follow that the mechanism of its action *in vivo* is exactly the same as that observed in the extract. All that can be concluded from such results is that there exists the probability that reactions observed in tissue extracts proceed in the same or relatively similar manner in intact organisms.

The foregoing is an over-simplified and in some respects rather idealized view of the general method by which progress is made in biological research. It assumes that, in order to comprehend a biological picture, one must first glimpse the picture in its entirety, then break it down and determine its components, and then reassemble it again in terms of its individual components. The last step is, of course, the most difficult and it may be contended that there exists a definite limit to our ability to integrate our knowledge of biological processes. For try as we may to approximate more and more closely what is actually happening in intact tissue, we must finally reach the point where any efforts of observation will alter the normal processes which are being investigated.

IV. Hygroscopic Equilibrium

Moisture is by far the predominant factor in determining the degree of biological activity in cottonseed. Even though, as will be shown later, there are other contributing factors, their effect is superimposed upon the

effect of moisture; therefore, other factors serve to modulate but never to supersede in importance the effect of moisture. Cottonseed will assume a moisture content in equilibrium with that of the surrounding atmosphere. Relative humidity, therefore, exerts a very great influence on the degree of biological activity in the seeds. For this reason, the nature of the hygroscopic equilibrium of cottonseed and the rate at which it is attained is of considerable importance.

Moisture content is commonly reported on either a wet basis (*per se* or as received) and a dry basis (moisture-free). Values for moisture, calculated on one basis, may be converted to the other by means of the following formulas:

$$\text{per cent moisture (wet basis)} = \frac{\text{per cent moisture (dry basis)}}{100 + \text{per cent moisture (dry basis)}} \times 100$$

$$\text{per cent moisture (dry basis)} = \frac{\text{per cent moisture (wet basis)}}{100 - \text{per cent moisture (wet basis)}} \times 100$$

Thornton and Briggs [7] determined the effect of the relative humidity of air circulating through cottonseeds on the rate of absorption of moisture by the seed. Their experiments were of a relatively short duration (165 to 180 hours), and except in the case where air of low relative humidity was used, equilibrium was not attained. Thornton and Bishop [8] attempted to attain equilibrium by using static air. Here too, equilibrium was not attained at the end of 675 hours, and the only conclusion that could be drawn was that the rate of absorption of moisture increased with the increase in the temperature of the air. Equilibrium moisture values which were obtained by these authors for kernels, cake, and meal are given in Table 37.

Franco [9] determined the hygroscopic equilibrium of the I.A. 7387 variety of cottonseed grown in the state of São Paulo, Brazil. His experiments were conducted at an average temperature of 19° C. and lasted twenty days, the period required to assure attainment of equilibrium. Simpson and Miller [10] determined the equilibrium moisture values for the Stoneville variety of cottonseed. Their experiments were conducted at 25° C. for twelve weeks. Karon [11] investigated the hygroscopic equilibrium of the D & PL 45 variety of intact cottonseed, meats, and hulls at 26° C. His observations extended over thirty-six days, although equilibrium was attained in most samples after eight days. The results of the analyses of Franco (calculated on a wet basis),[9] Simpson,[10] and

[7] M. K. Thornton, Jr., and P. P. Briggs, *Oil Mill Gazetteer,* **33,** No. 6, 15–26 (1929).
[8] M. K. Thornton, Jr., and F. F. Bishop, *Oil Mill Gazetteer,* **42,** No. 12, 11–15, 27–31 (1938).
[9] C. M. Franco, *Bragantia,* **3,** 137–149 (1943).
[10] D. M. Simpson and P. R. Miller, *J. Am. Soc. Agron.,* **36,** 957–959 (1944).
[11] M. L. Karon, *J. Am. Oil Chemists' Soc.,* **24,** 56–58 (1947).

Karon [11] for intact cottonseed are given in graphic form in Figure 22. It should be noted that, although Franco's experiments were conducted at a lower temperature, his results coincide with those of the others. It also should be mentioned that he determined the moisture content in the seeds

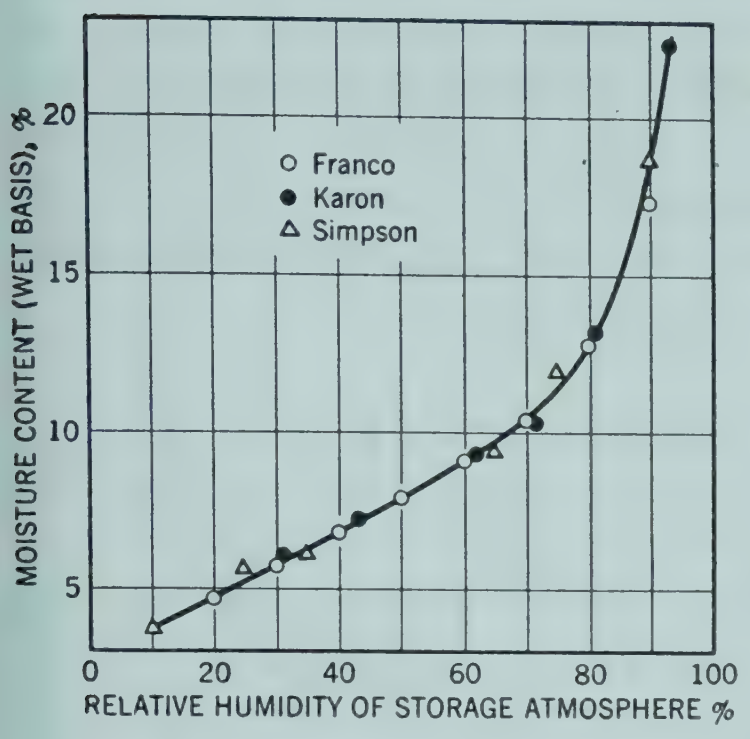


Fig. 22. Relation of moisture content of cottonseed to relative humidity of storage atmosphere (according to data of Franco,[9] Simpson,[10] and Karon[11]).

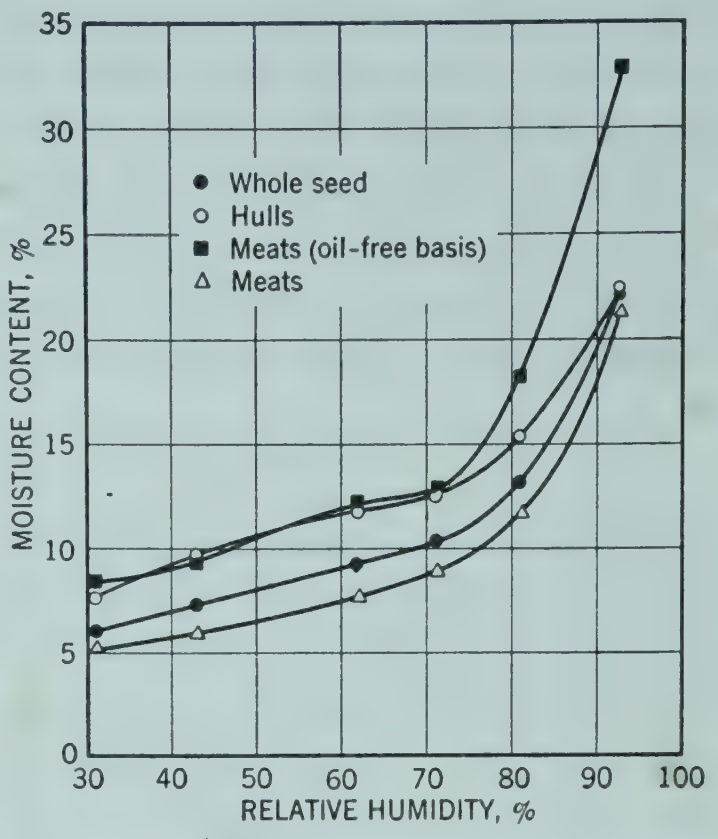


Fig. 23. Relation of moisture content (wet basis) of the whole cottonseed, meats, and hulls to relative humidity of the storage atmosphere.[11]

TABLE 37

Hygroscopic Equilibrium of Cottonseed Kernels, Cake, and Meal at 34°C.[a]

Relative humidity, %	Moisture content (wet basis), %		
	Kernels	Cake	Meal
30	5.25	8.5	7.76
50	9.00	13.5	12.25
85	10.25	14.5	15.5

[a] M. K. Thornton, Jr., and F. F. Bishop, *Oil Mill Gazetteer*, **42**, No. 12, 11–15, 27–31 (1938).

by drying at 110° C. for forty-eight hours in a convection oven.[12] Both the temperature and duration of the drying period were in this case greater than is required in the official methods for moisture analysis.

Moisture is not distributed evenly throughout the cottonseed; the hulls contain more than the average for the entire seed, whereas the meats have less than average. Barrow [13] has published the values obtained by averag-

[12] C. M. Franco, *private communication* (1946).
[13] E. H. R. Barrow, *Ind. Eng. Chem.*, **7**, 709–712 (1915).

ing the results of thousands of analyses of whole cottonseeds, meats, and hulls. An average moisture content of 11.42% in the seeds was found to correspond to 13.82 and 9.48% in the hulls and meats, respectively; an average of 10.29% in the seeds corresponded to 13.02% in the hulls and 8.17% in the meats; and an average of 9.51% in the seeds corresponded to 11.96% in the hulls and 7.58% in the meats. The distribution of moisture in the meats and hulls over a wide range of moisture contents is given [11] in Figure 23. At very high moisture contents, the moisture becomes evenly distributed throughout the seed. If, however, the moisture content of the meats is calculated on an oil-free basis, both the hulls and the meats have the same moisture contents when they are in equilibrium

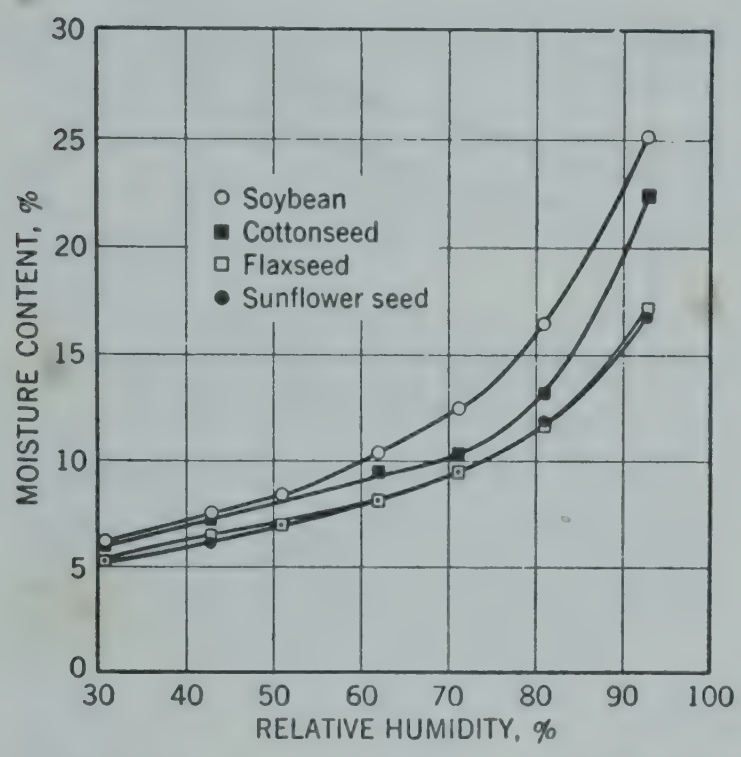


Fig. 24. Comparison of the hygroscopic equilibrium (wet basis) of cottonseed, flaxseed, soybeans, and sunflower seed (from the data of Karon[11] and Larmour, *et al.*[15]).

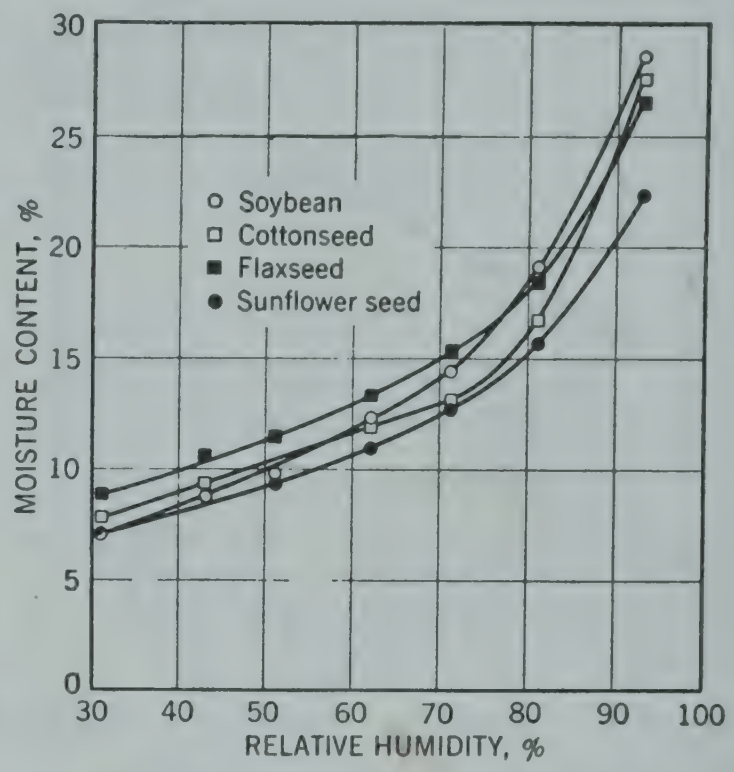


Fig. 25. Comparison of the hygroscopic equilibrium (wet basis) of cottonseed, flaxseed, soybeans, and sunflower seed, calculated for the oil-free seeds.[11]

with an atmosphere having a humidity in the range of 30–70%. At higher humidities, the meats absorb much more moisture than do the hulls.

A calculation of moisture content in meats on an oil-free basis rests on the assumption that only an insignificant portion of the moisture in the meats is to be found in their oleaginous regions. The moisture content of the lyophilic portion of the seed would, therefore, be much greater than would be indicated on the basis of total weight. On this basis Bailey [14] explained the difference between the intensity of respiration of flaxseed and cereal grains of equivalent over-all moisture content. A comparison of the hygroscopic equilibrium values at 25–26° C. for cottonseed, soybean, flaxseed, and sunflower seed is given [11, 15] in Figure 24, and the same

[14] C. H. Bailey, *Plant Physiol.*, **15,** 257–274 (1940).
[15] R. K. Larmour, H. R. Sallans, and B. M. Craig, *Can. J. Research,* **F22,** 1–8 (1944).

data calculated by Karon [11] on an oil-free basis are given in Figure 25. Inasmuch as the seat of most biological activity is in the lyophilic portion of the seed, the latter graph gives a truer representation of the effective moisture content in hygroscopic equilibrium with the atmosphere.

V. Germination

Biological processes occurring in germinating seeds in many respects are the same as or similar to those which occur at much slower rates in resting seed. An understanding of the activity and changes which occur during germination may contribute much to the knowledge of the biological reactions occurring to a lesser extent in stored cottonseed.

A. Methods of Testing Germination

In the standard technique for germinating cottonseed,[16] dry seeds are put between folds of moist cotton flannel or absorbent paper towelling and placed in the germination chamber which is maintained alternately at 20° and 30° C. Each day the seeds are subjected to a temperature of 30° C. for six to eight hours, and of 20° C. for the remainder of the day. Sprouted seeds are counted and removed on the third and fifth days and the test is considered completed at the end of seven days. Seeds which do not reveal a high percentage of germination under these conditions may give improved results if they are prewetted, *i.e.*, first soaked in water until the fuzzy or short lint is wet and then placed in the moist substrata for germination.[17]

Delinting with sulfuric acid generally facilitates the germination by removing external contamination and making possible a more rapid penetration of water into the seeds. In order to increase further the rapidity with which water enters the seeds, Simpson, Adams, and Stone [18] proposed the following testing procedure:

(*a*) The seed samples are first delinted with sulfuric acid and thoroughly washed and dried. (Delinting is accomplished by dipping the seeds in concentrated sulfuric acid for three minutes.)

(*b*) The delinted seeds are placed in a suitable container and covered with water. The aperture of the container is then attached to a suction line and the contents subjected to a vacuum of 27 inches of mercury for five minutes.

(*c*) The seeds are removed from the container, drained of surplus water, and placed immediately on moist paper towelling.

Surface sterilization will control mold growth and decay during germi-

[16] D. M. Simpson, *Handbook on Seed Testing,* Association of Official Seed Analysts of North American, Washington, 1939.

[17] E. H. Toole and P. L. Drummond, *J. Agr. Research,* **28,** 285–292 (1924).

[18] D. M. Simpson, L. Adams, and G. M. Stone, *U.S. Dept. Agr. Tech. Bull.,* **734** (1940).

TABLE 38

Dormancy of Cottonseed during the Period of Boll Opening at U.S. Acclimatization Field Station, James Island, South Carolina, 1932[a]

Date picked (Oct., 1932)	Moisture in seeds, % (wet basis)	Percentage of fresh seeds germinated after indicated number of days in germinator																Percentage of seeds germinated after drying and storing for one month after indicated number of days in germinator			
		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	*Total*	4	5	7	*Total*
Tidewater variety (tagged October 5)																					
5	53.9				3			1						1			5		79	1	80
6	53.1			2			7							10		5	24		82	6	88
7	52.2		2			5			2				4		3		16		77	6	83
8	48.2			3				7				6		5			21		87	1	88
9	33.0			3			6				9		5				23		87	5	92
10	37.8					19				4		2					25		86	3	89
11	24.5			33		11			9			3					56		81	9	90
12	15.8		10				57	3		7							77		85	9	94
13	11.3	31				47	7										85		93	4	97
14	13.7	10		18		38		12									78		78	6	84
Sea Island variety (tagged October 5)																					
5	48.4				85			7									92	96		0	96
6	48.2			70			24							1			95	97		0	97
7	49.0		58			31							4				93	96		0	96
8	41.2			69				20				2					91	94		1	95
9	29.4			89			8										97	96		0	96
10	20.2		89			1											90	97		1	98
11	17.1			87		3											90	91		6	97
12	13.9		95														95	92		0	92
13	12.3	89				2											91	92		0	92
14	13.8	96		2													98	97		0	97

[a] D. M. Simpson, *J. Agr. Research*, **50**, 429–434 (1935).

nation of more sensitive seeds. Sterilization of this type can be easily accomplished by soaking the seeds in a calcium hypochlorite solution (5 g. of calcium hypochlorite in 150 ml. of water) for one hour [19] or in a 0.1% solution of mercuric chloride for one-half hour. Chester [20] has proposed a simple method for differentiating sound and unsound seeds. His method consists of delinting the seeds with acid, after which they are placed in a suitable container and covered with water. The seeds which float are rejected. It was found that nearly all internally infected and weak seeds could be removed by this means. Arndt,[21] however, found that the relative proportions of light and heavy seeds were determined more by varietal characteristics than by viability, internal infection by fungi, or crop year. He therefore questioned the general applicability of the above method for improvement of seed quality.

B. Dormancy

Cottonseeds from freshly opened bolls usually do not germinate as promptly as do normal dry seeds. Simpson [22] found that fresh seeds of the Upland species from bolls which had been opened one to five days germinated very slowly, and a considerable percentage of sound seeds did not germinate even after twenty-four days in the germinator. Complete germination usually occurs in normal dry seeds in from five to seven days in the germinator. This lack of germinating power may be remedied by drying the fresh seeds and storing them for a month. Drying alone will not suffice, according to Simpson,[22] who cites an example wherein fresh seeds had a germination percentage of 12, dried seeds of the same lot had a germination of 75, and dried seeds which had been stored for one month after drying, 84. Fresh Sea Island species of cottonseed, however, exhibit no such reduced germination, although even for this species there is some improvement in the speed of germination after drying and storage (see Table 38).

Dormancy is a phenomenon common to most seeds and is due to both physical and biological factors.[23] Seeds may have a hard coat which prevents the intake of water and the exchange of respiratory gases (oxygen and carbon dioxide). In other cases the embryos are immature and require several weeks or months before they become sufficiently developed to germinate. Even if to all appearances the embryos are mature, certain biological changes must occur before germination can take place. Cottonseed which exhibit a tendency for delayed germination germinate completely in two days when the seed coats are removed. On the basis of these

[19] J. K. Wilson, *Am. J. Botany,* **2,** 420–427 (1915).
[20] K. S. Chester, *Phytopathology,* **28,** 745–749 (1938).
[21] C. H. Arndt, *Phytopathology,* **35,** 747–753 (1945).
[22] D. M. Simpson, *J. Agr. Research,* **50,** 429–434 (1935).
[23] E. C. Miller, *Plant Physiology,* 2nd ed., McGraw-Hill, New York, 1938.

experiments, Simpson *et al.*[18] believe that dormancy may be a condition imposed upon the embryo by the seed coat.

C. Longevity

The longevity of sound seeds, *i.e.*, the length of time that they may be stored without losing viability, is dependent, other things being equal, upon their storage environment. The principle factors involved are the moisture content of the seeds during storage and the temperature of storage. A thorough investigation of the effects of various combinations of these two factors was undertaken by Simpson [24] with results on two Upland varieties as shown in Figure 26. It is clear from these results that

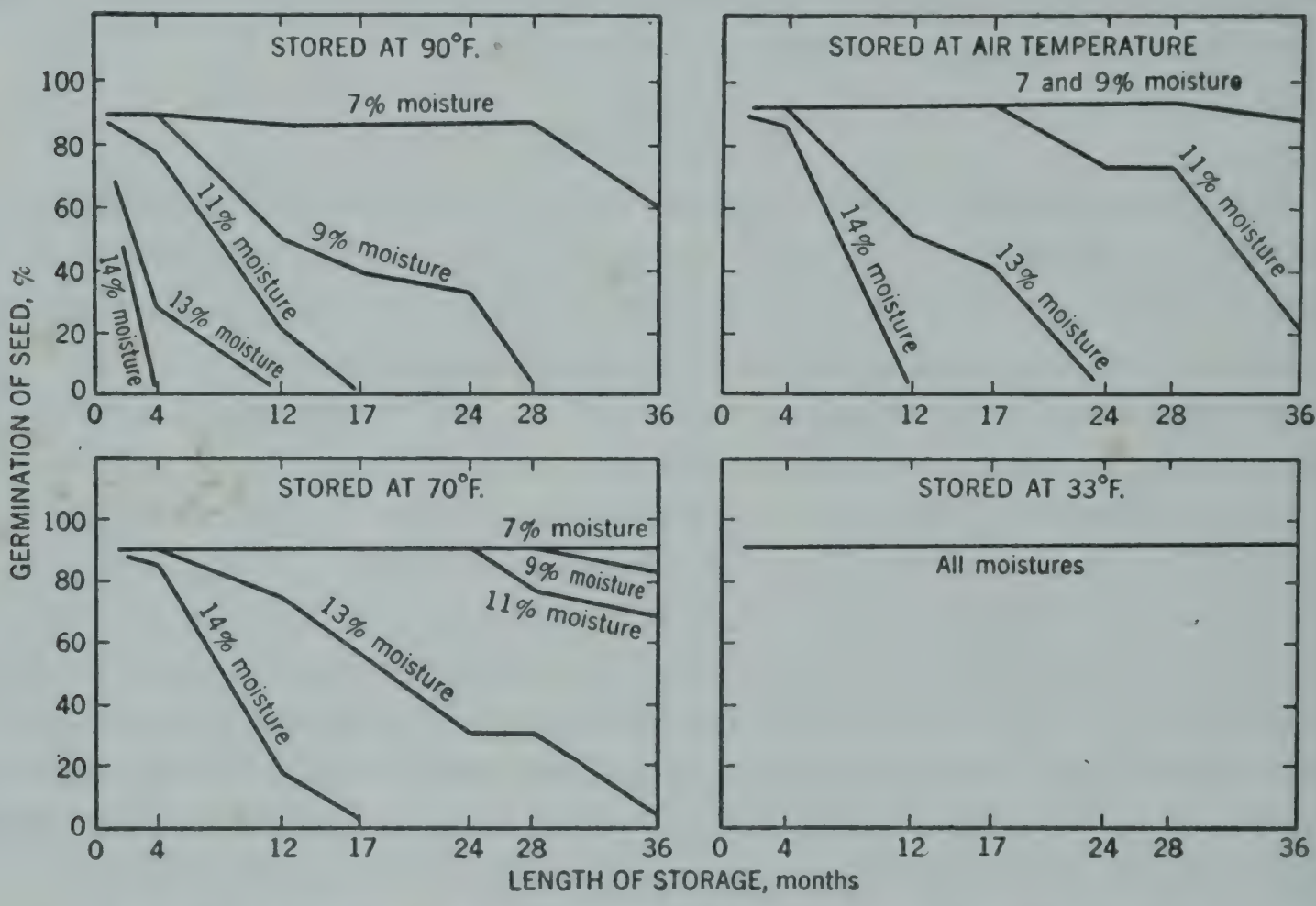


Fig. 26. Longevity of cottonseed as a function of moisture content and temperature of storage.[24]

when the moisture content is maintained at 7% the seeds will retain their viability for over two years even at temperatures as high as 90° F. At refrigerator temperatures (33° F.), seeds with moisture contents up to 14% may be stored for as long as three years without loss of viability.

Phillis and Mason [25] determined the effect of storage under conditions of extreme desiccation on the longevity of cottonseed and found that such conditions were almost as harmful as high moisture. Seeds were stored in desiccators above sulfuric acid solutions for control of the humidity, at temperatures which ranged from 75–85° F., with the

[24] D. M. Simpson, *J. Agr. Research*, **64**, 407–419 (1942).
[25] E. Phillis and T. G. Mason, *Ann. Botany*, **9**, 353–359 (1945).

results shown in Figure 27. It is surprising to note that seeds stored in an absolutely dry condition began to lose viability after eighteen months, and those stored at a relative humidity of 10%, which corresponds to a moisture content in the seed of about 2% (wet basis), deteriorated more rapidly than those stored at 50% relative humidity. Optimum conditions of storage were observed to lie in the range of 20–40% relative humidity, corresponding to 5–7% moisture content (wet basis) in the seed.

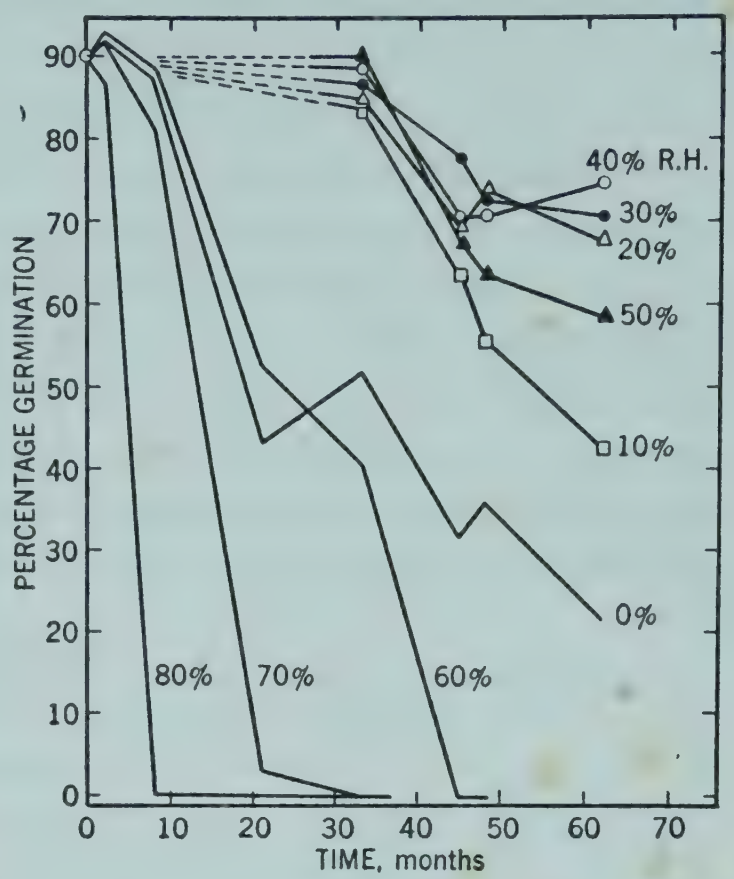


Fig. 27. Effect of extreme desiccation on longevity of cottonseed stored at 75–85° F.[25]

It is common commercial practice to store seeds for planting in bags which are not protected from variations in atmospheric humidity or temperature. At best, the air around the bags is circulated to minimize extremes of high humidity or temperature. In order to obtain information about the longevity of cottonseed in commercial storage, Simpson [26] conducted an investigation of the effect of climate on the viability of stored seeds. As a result of his investigations, he divided the cotton-growing areas of the United States into four zones, as shown in the accompanying table.

Arndt [27] pointed out that the longevity of seeds varies with the variety and year of harvest. In one experiment involving storage at room tem-

Zone	Representative locations	Probable length of safe storage, years
Lower Coastal Plains	Baton Rouge, La.	1 to 2
Upper Coastal Plains and adjacent interior	Florence, S. C. State College, Miss. Clemson, S. C. Greenville, Tex.	3 to 4
Northern rim of Cotton Belt	Jackson, Tenn. Knoxville, Tenn.	5 to 6
Southwestern dry land and irrigated areas	Sacaton, Ariz.	15 to 20

[26] D. M. Simpson, *J. Am. Soc. Agron.*, **38**, 32–45 (1946).
[27] C. H. Arndt, *private communication* (1946).

perature of cottonseed of 8–10% moisture content, one variety maintained good viability for sixty-six months, another for fifty-four months, and others, forty-two months. A period of five years appeared to be the maximal time that seeds may be expected to retain their viability in his laboratory (Clemson, South Carolina).

D. Effect of Sterilization

In some cotton-growing areas state or federal regulations require that all cottonseed be sterilized by means of heat to prevent the spread of the pink bollworm. These regulations require that the seeds be heated to a temperature in the range of 150–165° F. for thirty seconds. McDonald and Scholl,[28] and Del Curto [29] investigated the effect of heating seeds at various temperatures and concluded that sterilization under the prescribed conditions does not injure their viability as is evident from the results of several hundred comparative tests which are summarized in Table 39.

TABLE 39

Effect of Temperature to Which Cottonseeds Are Heated on Percentage of Germination[a]

Temperature to which seeds are heated, °F.[b]	Germination, %	
	Heated seeds	Unheated controls
139–144	78.5	77.4
145–149	72.8	72
150–154	75.6	78.6
155–159	62.5	67
160–164	82	82
165–170	78.5	69.5
170–up	10	69

[a] R. E. McDonald and G. J. Scholl, *Texas Dept. Agr. Bull.*, **71** (1922).

[b] These are the exit temperatures as the seeds leave the sterilization apparatus. The length of time it takes the seeds to reach these temperatures will vary with the equipment and the operating conditions.

E. Relationship between Free Fatty Acid Content and Viability

Simpson [24] found that seeds containing more than 1.8% free fatty acids failed to germinate and samples approaching that level germinated poorly and produced weak seedlings. Similar results were obtained by Rusca and Gerdes.[30] As a result of findings of this type, attempts have been made to substitute the relatively rapid free fatty acid determination for the

[28] R. E. McDonald and G. J. Scholl, *Texas Dept. Agr. Bull.*, **71** (1922).
[29] J. M. Del Curto, *Texas Dept. Agr. Bull.*, **86** (1927).
[30] R. A. Rusca and F. J. Gerdes, *U.S. Dept. Agr. Circ.*, **651** (1942).

time-consuming germination test as an estimate of viability. On the basis of the author's experiences [31] wherein it has been found that seeds with free fatty acid contents up to 11% exhibited appreciable percentage germination, it is felt that there is little or no basis for such a correlation. While, in general, it should be expected that seeds containing more than 2% free fatty acids would have a low percentage viability, there are sufficient exceptions to demonstrate that the best test for cottonseed viability is the germination test itself.

F. Changes during Germination

1. Respiration

Carbon dioxide is evolved in considerable quantities during germination. Simpson *et al.*[18] reported that germinating seeds kept at 30° C. for seventy-two hours evolved 120 mg. of carbon dioxide per gram of seedlings. This amount of gas at atmospheric pressure would have a volume equivalent to approximately 75 times the original volume of the seeds.

2. Constituents

During germination the total oil and total sugar contents of cottonseed decrease, the nitrogen content remains about the same, and the contents of free fatty acids and pentosans increase, as may be seen by reference to Table 40. There is a slight decrease in total content of phosphorus and a very marked increase in the percentage of the total phosphorus which is present as inorganic phosphorus. Thus, after germination for 0, 24, 48, 72, and 96 hours, the total phosphorus contents were 1.2, 1.4, 1.2, 1.1, and 1.1%, respectively, and the percentages of phosphorus in the inorganic form were 10.0, 11.2, 24.9, 35.4, and 44.4%, respectively.[32] With the exception of folic acid and inositol, members of the vitamin B group increase in cottonseed during germination.[33]

3. Enzymes

It is to be expected that the surge of biological activity during germination would be a result of or would be accompanied by stimulation of enzyme activity. That this is the case is indicated by reference to some of the observed effects of germination on the activity of individual enzymes in the cottonseed, which are summarized in the following paragraphs.

(a) Lipase. This enzyme catalyzes the reaction:

$$\text{glyceride} + \text{water} \rightarrow \text{glycerin} + \text{free fatty acids}$$

[31] M. L. Karon and A. M. Altschul, *Plant Physiol.*, **19,** 310–325 (1944).
[32] T. D. Fontaine, W. A. Pons, Jr., and G. W. Irving, Jr., *J. Biol. Chem.*, **164,** 487–507 (1946).
[33] V. H. Cheldelin and R. L. Lane, *Proc. Soc. Exptl. Biol. Med.*, **54,** 53–55 (1943).

Olcott and Fontaine [34] reported that, although they were unable to demonstrate lipase activity in resting cottonseed, this enzyme could be readily detected in germinating seedlings. The lipase activity increased to 20.1 units [35] in 91 hours and remained at this value to the end of the germination test (139 hours). As was shown in Table 40, during the same 139-hour period, the free fatty acids in the oil increased from 1.8 to 20.3%, which would indicate that hydrolysis of the glycerides is an intermediate stage in the catabolism of the oil during germination.

TABLE 40

Changes in Cottonseed Composition Occurring during Germination as Found by (a) Olcott and Fontaine and (b) Malowan[a]

Length of germination, hrs.	Root length, cm.		Moisture content, %[b]	Oil content, %[c]	Free fatty acids, %[d]	Total sugars, %	Pentosans, %	Nitrogen, %
(a)	(a)	(b)	(a)	(a)	(a)	(b)	(b)	(b)
0	0	—	6	43.0	1.82	—	—	—
—	—	0–2.6	—	—	—	3.50	5.32	6.44
23	0	—	48	43.5	1.52	—	—	—
42	1–2	—	63	45.2	5.45	—	—	—
67	2–5	—	73	37.9	8.53	—	—	—
—	—	2.6–8.5	—	—	—	2.81	6.02	6.02
91	5–8	—	78	33.2	11.47	—	—	—
—	—	8.5–13	—	—	—	1.91	7.03	6.19
115	8–15	—	83	25.0	15.22	—	—	—
139	10–18	—	84	22.8	20.32	—	—	—

[a] H. S Olcott and T. D. Fontaine, *J. Am. Chem. Soc.*, **63,** 825–827 (1941). J. Malowan, *Cotton Oil Press*, **5,** No. 4, 40–43 (1921).
[b] Moisture content recorded on wet basis (*per se*).
[c] Oil content on basis of dry material.
[d] Free fatty acids as per cent oleic.

(b) Catalase and Peroxidase. Both of these enzymes react with hydrogen peroxide. Catalase will decompose hydrogen peroxide as follows:

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$

while peroxidase utilizes it for further oxidation according to the example:

$$\underset{\text{Pyrogallol}}{2\,C_6H_6O_3} + 3\,H_2O_2 \rightarrow \underset{\text{Purpurogallin}}{C_{11}H_8O_5} + CO_2 + H_2O$$

In his classic report on the discovery of catalase, Loew [36] stated that cottonseed contained considerable quantities of this enzyme. Some of this catalase was found to be easily extractable by neutral or slightly alkaline

[34] H. S. Olcott and T. D. Fontaine, *J. Am. Chem. Soc.*, **63,** 825–827 (1941).
[35] Expressed as percentage of Wesson oil hydrolyzed by 17 mg. of germinated cottonseed (calculated on oil- and moisture-free basis) in 16 hrs. at *p*H 7.2.
[36] O. Loew, *U.S. Dept. Agr. Rept.*, **68** (1901).

buffer solutions, but a considerable quantity remained in the extracted residue. Olcott and Thornton [37] confirmed Loew's observation and added that cottonseed is one of the best plant sources of this enzyme. They found that during the first forty-eight hours of germination the catalase concentration of seedlings increased 120 to 140%.

The effect of germination on the extractable and total catalase and peroxidase in cottonseed is shown in Table 41. It is interesting to note that after the second day of germination the total catalase concentration decreases and the extractable catalase decreases even more rapidly.

TABLE 41

Effect of Germination on the Catalase and Peroxidase Content of Cottonseed[a]

Length of germination period, days	Catalase activity		Peroxidase activity		Ratio of activities	
	T	*E*	*T*	*E*	$\frac{T \text{ (catalase)}}{T \text{ (peroxidase)}}$	$\frac{TE \text{ (catalase)}}{TE \text{ (peroxidase)}}$
0	214.4	85.1	1.34	56.1	160	242.6
2	271.8	39.6	1.58	60.8	172	111.9
3	95.6	3.3	3.77	53.4	25.3	10.8
6	56.7	4.4	5.20	36.9	10.9	1.3
7	47.7	7.9	2.25	28.1	21.2	5.9

[a] *T* is the monomolecular rate constant for reaction conducted at 30°C., expressing total activity of one gram of material. *E* is the per cent of total activity found in a neutral dilute buffer extract.

VI. Heating

The most readily observed and measured biological activity in resting seeds is the production of heat. Heating can be observed in the interior of a bushel measure of moist corn, in sacks of flaxseed, in a truckload or carload of cottonseed, in large seedhouses, and in small seed piles. When seed of sufficiently high moisture content is stored in quantities large enough to provide thermal insulation for the material in the interior, a rise in temperature will ultimately be observed.

Moist cottonseed when stored in bulk will heat relatively rapidly, and in such seed temperatures as high as 190° F. have been recorded. Unduly high temperatures may result not only in damage to the seed, but also to the seedhouse. However, by far the greatest losses result from the damage to the seed through acceleration of biochemical processes which proceed more rapidly at elevated temperatures. Heating accelerates damage due to oxidation of the pigments, lipolysis, protein deterioration, loss in viability, etc.

[37] H. S. Olcott and C. D. W. Thornton, *J. Am. Chem. Soc.*, **61,** 2417–2418 (1939).

A. Methods of Measurement

Various types of containers have been used for inducing heating and measuring the degree of heating in seeds. For example, Malowan [38] used a wooden box insulated on all sides by a one-foot layer of hulls. Others have observed the heating of seeds kept in Dewar flasks and crocks; Ramstad and Geddes,[39] Sallans, Sinclair, and Larmour,[40] and Milner [41] used an adiabatic calorimeter for observing the heating of soybean, flaxseed, and sunflower seeds. Adiabatic calorimeters for this type of investigation are so constructed that the temperature gradient between the seeds and the surrounding air is less than 0.1° C. As the seeds heat, the outside temperature is automatically raised to maintain this gradient. The advantage of such an arrangement is that the heating pattern of the seeds may be determined uncomplicated by the heat losses that are likely to occur in less refined equipment.

B. Effect of Moisture

Malowan [38] demonstrated that the rate of heating and the maximum temperature reached increase with the moisture content of the seeds. Neither the application of pressure amounting to 200 pounds per square foot nor natural ventilation had any appreciable effect on the rate of heating, but these factors did have some influence over the rate of cooling as is shown in Table 42. It should be noted that the rate of aeration actually has a very definite influence upon the rate and intensity of heating as was pointed out by Milner.[41] The natural conditions of ventilation maintained by Malowan in the above-mentioned experiments were probably not adequate to demonstrate the stimulatory effect of aeration.

C. Patterns of Heating during Storage

1. Storage without Forced Aeration

An example [42] of the pattern of heating of cottonseed maintained in a rather small pile in a sealed tank is given in Figure 28. The seed used in this experiment had an original moisture content of 14.9% (wet basis); after storage for 170 days the moisture had decreased to 11.9%. In the same period the free fatty acid content increased from 4.3% to about 30%. The temperature of the seed rose very rapidly at the beginning of

[38] J. Malowan, *Cotton Oil Press,* **4,** No. 11, 47–49 (1921).
[39] P. E. Ramstad and W. F. Geddes, *Minnesota Agr. Expt. Sta. Tech. Bull.,* **156** (1942).
[40] H. R. Sallans, G. D. Sinclair, and R. K. Larmour, *Can. J. Research,* **F22,** 181–190 (1944).
[41] M. Milner, *Doctoral Dissertation,* University of Minnesota, 1945.
[42] A. M. Altschul, M. L. Karon, L. Kyame, and M. Caravella, *Oil & Soap,* **20,** 258–263 (1943).

the storage period and then decreased slowly and unevenly. Several times during the storage period the seeds showed a tendency to heat again, with the result that the cooling curve has a wavy form with progressively lower maxima as the period of storage was prolonged. The intervals between

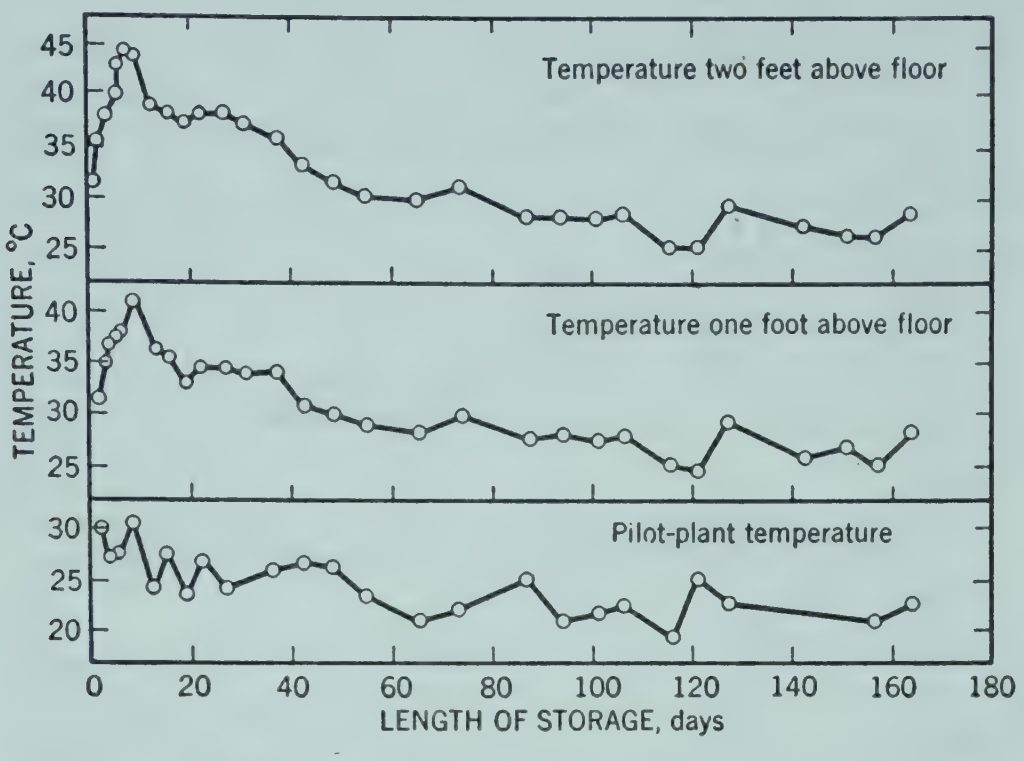


Fig. 28. Heating pattern of unventilated cottonseed.[42]

maxima did not coincide with the fluctuation in the surrounding air temperature; they must, therefore, be considered an intrinsic characteristic of the heating process.

TABLE 42

Effect of Moisture, Ventilation, and Pressure on Heating of Cottonseed[a]

Test conditions		Moisture content (wet basis)		Temperature, °F.			
Ventilation	Pressure	Initial, %	Final, %	Initial, %	Maximum	Final (after 37 days)	External air
None	None	13.4	12.4	77	117 in 27 days	116	60–70
None	Used		12.5		116 27	116	
Used	None		11.4		115 36	115	
Used	Used		11.1		115 35	115	
None	None	16.6	16.0	60	129 in 29 days	115	40–66
None	Used		16.2		129 29	112	
Used	None		14.5		129 27	110	
Used	Used		16.3		127 26	106	
None	None	28.2	14.2	70	155 in 7 days	129	60–75
None	Used		18.5		141 11	136	
Used	None		12.5		155 7	103	
Used	Used		15.5		157 8	131	

[a] J. Malowan, *Cotton Oil Press*, **4**, No. 11, 47–49 (1921).

2. Storage with Forced Aeration

Further information relative to the heating process is supplied by the temperature patterns of seeds stored in 30-ton lots under conditions where forced aeration was applied whenever the temperature became excessive. Such patterns are shown in Figure 29. In the first of these experiments

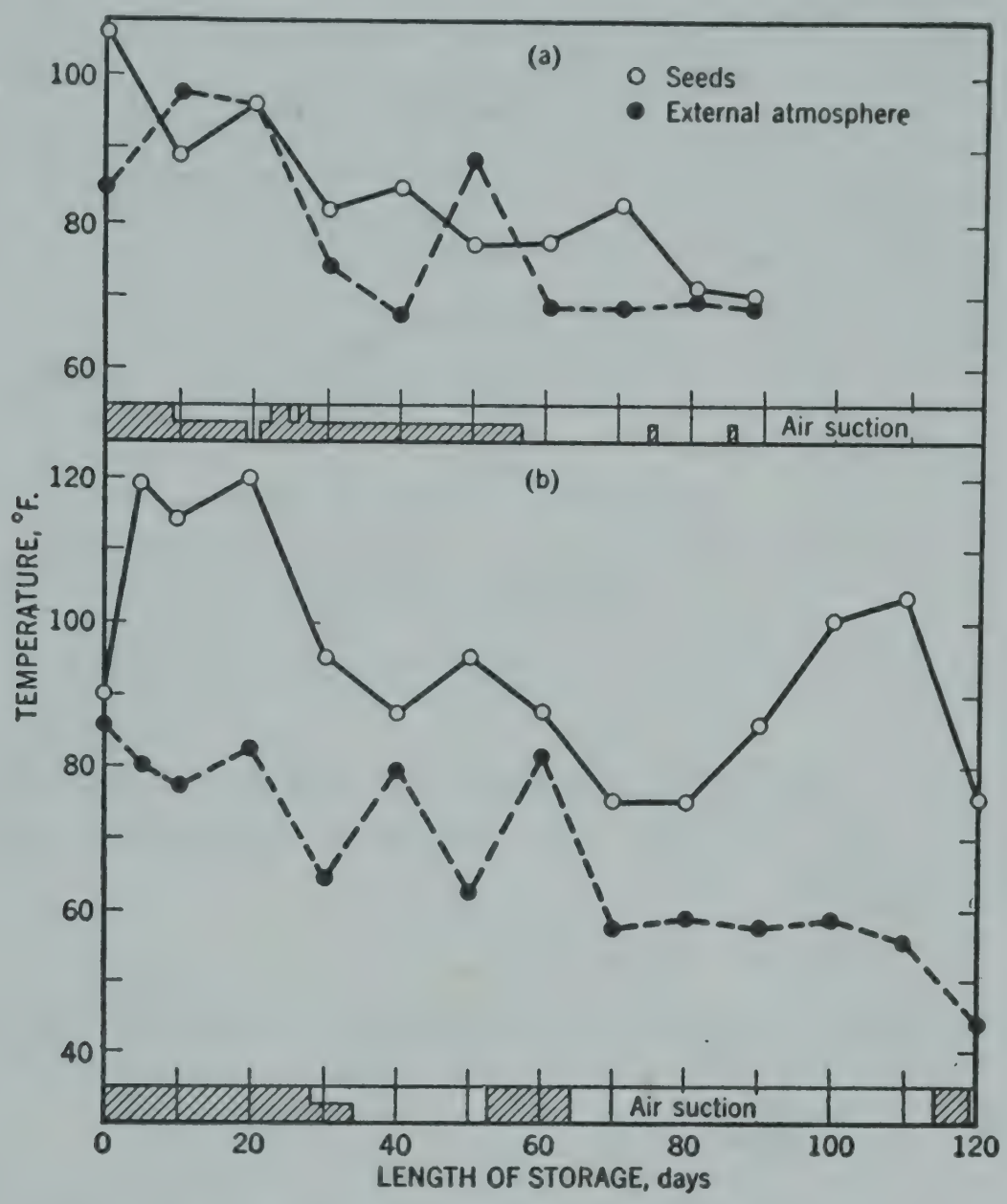


Fig. 29. Heating patterns of ventilated cottonseed. The shaded areas represent periods when air suction was applied; the relative height of the shaded portion denotes the fraction of each day during which the suction fan was operated.

(Part (a) of the figure), the seeds had an original moisture content of 13.6% (wet basis) and a free fatty acid content of 7.0%. After storage for three months the seed had an average moisture content of 10.6% and a free fatty acid content of 12.0%. In the second experiment (part b of the figure), the initial moisture and free fatty acid contents were 19.9 and 1.7%, respectively, and the final values after four months' storage were 12.6 and 6.0%, respectively.

The seeds in these experiments heated repeatedly and were cooled by aeration just as frequently during the storage period, which is noteworthy

because even after their moisture contents had been markedly reduced as a result of the aeration, they maintained the ability to reheat. The initial rise in temperature observed in both experiments at the onset of aeration was undoubtedly due to the stimulation of heating as a result of the removal of respired carbon dioxide from the vicinity of the seed and replacement of it with fresh air. The first result of aeration, therefore, is to stimulate biological activity so that heat is produced faster than it can be removed by the current of air. Eventually, the temperature is reduced, and the biological activity decreases to a point where still further cooling is favored, and the temperature of the seed pile decreases. It should be noted that in these experiments considerable amounts of free fatty acids were formed in the seeds despite the forced aeration and the relatively low temperatures at which they were maintained during most of the storage period.

D. Effect of Storage Atmosphere

Based upon the assumption that the presence of oxygen is a prerequisite to heating, numerous attempts have been made to minimize such activity by the substitution of inert gases in the atmosphere surrounding the seed.

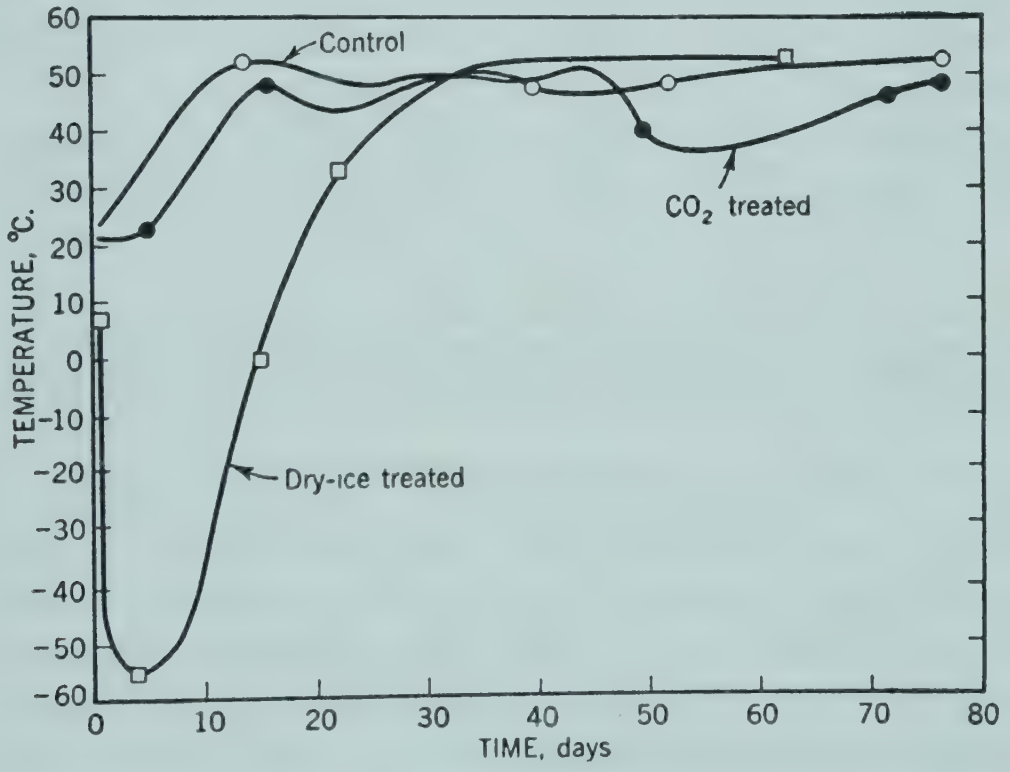


Fig. 30. Effect of carbon dioxide on the heating of cottonseed.[43]

The use of nitrogen has been reported as being ineffective in controlling heating. Carbon dioxide has been shown to be relatively ineffective in pilot plant scale tests.[43] Two methods of carbon dioxide treatment were tried: (*a*) the gas was introduced into the top of a tank containing a ton of moist cottonseed and allowed to diffuse throughout the pile; and

[43] G. Heinemann, *private communication* (1944).

(*b*) alternate layers of moistened seed and Dry Ice (solid carbon dioxide) were packed into a storage tank at the rate of 750 pounds of Dry Ice per ton of seed. Temperature measurements were made regularly with results as shown in Figure 30. Several times in the storage period, portions of the seed in each experiment was processed and the free fatty acid content of the oils determined with the result shown in Table 43.

The effect of treatment with Dry Ice is of particular interest because it demonstrates an important factor contributing to biological activity. In the course of this treatment, the seeds were frozen and following the dissipation of the Dry Ice they warmed up and thawed out with the result that many of the cells were no doubt broken. With the disruption of cellular

TABLE 43

Effect of Carbon Dioxide on Rate of Lipolysis of Cottonseed[a]

Experiment no.	Treatment	Moisture content, %[b]	Length of storage, days					
			0	7	30	40	65	80
			Free fatty acid content, %					
1	Control	17.7	0.5	0.5	2.0	4.1	6.3	8.7
2	Control	17.8	0.5	0.5	2.3	4.1	5.9	9.4
3	Gaseous carbon dioxide	17.2	0.5	0.5	2.4	4.0	6.1	9.4
4	Dry Ice	19.0	0.5	0.5	2.9	8.0	8.9	Seed removed

[a] G. Heinemann, *private communication* (1944).

[b] The seeds had an original moisture content of 10% (wet basis) but were artificially conditioned to these moisture contents before the experiment was begun.

organization the previously isolated cell contents became mixed and various types of enzymatic activity were stimulated. It was, therefore, to be expected that the seed treated in this manner would heat very rapidly to a temperature above that of the untreated seed, and that they would develop free fatty acids at a much greater rate than is usual in seed on the basis of their moisture content. This actually proved to be the case.

In view of the fact that the respiration of many seeds is inhibited by high concentrations of carbon dioxide,[14, 39] it might be expected that some inhibition of heating would follow the use of this gas to prevent deterioration of stored seed. Examination of the curves in Figure 30 shows that there was an initial lag of about ten days during which the temperature of the seed kept in an atmosphere of carbon dioxide did not rise as high as did that of the control. After that period there was no appreciable difference between the treated and control seeds, which is due in part to the

production of large amounts of carbon dioxide in the control seeds as a result of respiration. After storage for ten days the concentration of carbon dioxide in the atmosphere of the control seeds was probably sufficient to equal the effect due to the artificial addition of carbon dioxide to the treated seeds. Had the control lots of seeds been aerated during this experiment they would undoubtedly have heated to a higher temperature than did either the seeds of the control or the carbon dioxide treated lot.

The principle that removal of oxygen will inhibit heating is sound and was demonstrated by Malowan [38] who was able to inhibit cottonseed respiration drastically by displacing the air in the seed atmosphere by hydrogen. The value of the above-mentioned experiment with carbon dioxide lies, therefore, in the demonstration that, though in theory it should be possible to inhibit heating by removal of oxygen from the seed atmosphere, the achievement of such conditions on large quantities of seeds is a very difficult operation.

E. Heating of Meats and Hulls

Cottonseed meats and hulls will heat when their moisture content is raised sufficiently high and they are stored in insulated containers. To illustrate this fact, Malowan [38] compared the heating of whole cottonseed, meats, and hulls at 17, 16, and 35% moisture levels, respectively. The cottonseed reached a maximum temperature of 134° F. in eleven days, the meats a maximum of 125° F. in eight days, and the hulls were still increasing in temperature on the thirteenth day, at which time the temperature was 123° F. On the basis of information obtained on other types of seeds (corn [44] and sunflower seed [40]) it might be expected that meats will heat even more rapidly. These effects merely reflect the fact that any disturbance of the high degree of cellular organization existing in the intact seed will result in increased activity of exothermic biological processes.

F. Chemical Changes during Heating

Malowan [45] made extensive chemical analyses to determine the changes which occur in the seed, meal, and hull constituents of cottonseed during heating, with the results shown in Tables 44, 45, and 46. Neither oil nor protein are consumed in the heating process, the sole sources of energy being carbohydrates in the seeds or meats, and pentosans in the hulls. Apparently an intermediate stage in the combustion of carbohydrates consists of the production of reducing sugars, whose concentration increases temporarily during heating. Although there is no over-all loss in nitrogen, the proteins are partially hydrolyzed, as is indicated by the

[44] C. H. Bailey, *Minnesota Agr. Expt. Sta. Tech. Bull.*, **3** (1921).
[45] J. Malowan, *Cotton Oil Press*, **5**, No. 4, 40–43 (1921).

TABLE 44

Chemical Changes in Cottonseed during Heating[a]

Constituent	Length of storage, days				
	0	9	16	44	263
	Max. temp. 60°F.			Max. temp. 109°F.	
Moisture (wet basis), %	16.0	14.2	14.4	14.6	12.6
Total oil, %	17.7	17.2	16.3	17.2	17.5
Total nitrogen, %[b]	3.3	3.3	3.1	3.1	3.2
Magnesia nitrogen, %[b,c]	0.05	0.08	0.08	0.10	0.11
Nitrogen soluble in sodium chloride solution, %[b]	2.6	2.7	2.4	2.4	0.5
Total sugars, %[d]	2.1	2.5	2.2	2.2	0.4
Reducing sugars, %[d]	None	—	—	—	—
Pentosans, %[d]	12.1	11.4	12.3	12.8	15.2
Free fatty acids, %[e]	1.0	1.2	0.6	1.0	1.6

[a] J. Malowan, *Cotton Oil Press*, **5**, No. 4, 40–43 (1921).
[b] Determined on moisture-free meal.
[c] A measure of free or loosely bound ammonia.
[d] Determined on oil-free and moisture-free meal. Reducing sugars reported as dextrose.
[e] Percentage of free fatty acids in oil reported as oleic acid.

TABLE 45

Chemical Changes in Cottonseed Meats during Heating[a]

Constituent	Length of storage, days							
	0	5	20	63	77	112	133	255
	Maximum temperature, °F.							
	109	137	129	123	121	113	111	
Moisture (wet basis), %	22.1	17.5	16.2	16.2	14.6	11.5	10.0	8.9
Total oil, %	23.4	—	—	26.6	—	—	—	25.7
Total nitrogen, %[b]	4.7	4.9	5.3	5.2	5.4	5.8	5.9	6.1
Magnesia nitrogen, %[b,c]	0.08	0.09	0.15	0.18	0.18	0.17	0.18	0.19
Nitrogen soluble in sodium chloride solution, %[b]	3.7	3.9	1.0	0.9	1.0	0.9	0.9	0.9
Total sugars, %[d]	3.7	5.0	3.9	0.7	0.6	0.0	0.0	0.0
Reducing sugars, %[d]	0.0	1.1	1.2	0.4	0.1	0.0	0.0	0.0
Pentosans, %[d]	5.7	5.5	5.9	5.1	5.9	5.4	5.3	5.9
Free fatty acids, %[e]	1.7	9.0	18.7	25.7	25.1	31.4	33.5	48.8

[a] J. Malowan, *Cotton Oil Press*, **5**, No. 4, 40–43 (1921).
[b] Determined on moisture-free meal.
[c] A measure of free or loosely bound ammonia.
[d] Determined on oil-free and moisture-free meal. Reducing sugars reported as dextrose.
[e] Percentage of free fatty acids in oil reported as oleic acid.

TABLE 46

Chemical Changes in Cottonseed Hulls during Heating[a]

Constituent	Length of storage, days									
	0	14	36	64	106	180	240	323	471	522
	Maximum temperature, °F.									
	143	125	77	153	118					
Moisture (wet basis), %	24.5	21.5	17.2	15.8	25.0[b]	9.2	41.3[b]	45.1[b]	42.5[b]	40.4[b]
Total sugars, %[c]	0.0	0.0	1.1	None	—	—	—	—	—	—
Reducing sugars, %[c]	None	—	—	—	—	—	—	—	—	—
Pentosans, %[c]	24.1	26.2	25.4	27.7	23.8	25.0	11.8	10.1	6.3	5.7
Free fatty acids, %[d]	0.4	0.3	0.1	0.1	0.4	0.2	—	—	—	—

[a] J. Malowan, *Cotton Oil Press*, **5**, No. 4, 40–43 (1921).
[b] Moisture was again added to the hulls to induce further heating.
[c] Determined on oil-free and moisture-free hulls.
[d] Reported as oleic acid.

increase in ammonia nitrogen; moreover, they are denatured, as is indicated by their diminished solubility in salt solutions.

The observations of Malowan have been confirmed by others and, in addition, it has been shown that there is a decrease in organic phosphorus. In seeds which had an original ratio of organic to inorganic phosphorus of 23.3, this ratio was reduced to 7.4 by raising their moisture content to 17% and allowing them to heat for thirty-seven days. In the same period the free fatty acid content increased from 0.6 to 27%. The principal difference between the chemical changes which take place during germination and those that occur during heating is that the oil content decreases during germination where as it remains constant during heating.

VII. Respiration

A. Definition

Respiration has been defined as a process which proceeds in every living cell with the liberation of energy in a form that is available to the protoplasm.[23] In the presence of oxygen as the oxidizing agent, organic foodstuffs are oxidized to form water and carbon dioxide as the ultimate products. Oxidation, however, can take place in living material without the participation of gaseous oxygen, *i.e.*, under anaerobic conditions. Under such conditions some of the organic substances can themselves act as the

oxidizing agents so that the cellular constituents undergo an over-all internal oxidation and reduction, a process which is generally referred to as fermentation or glycolysis.

B. Anaerobic and Aerobic Respiration in Cottonseed

There is little known concerning anaerobic respiration in cottonseed although this phenomenon is known to occur in many, and probably occurs in all plants.[23] The author has detected strong odors of alcohol emanating from samples of cottonseed stored in tightly packed closed containers. Anyone familiar with the odor of the exhaust air from a seed-house fan will have detected the alcoholic odor characteristic of fermentation. It is conceivable that in large seed piles there are regions where anaerobic conditions prevail, so that fermentation may readily occur. Considerably more is known concerning the aerobic respiration of cottonseed, and all further references in this chapter to respiration will be to respiration of this type.

C. Methods of Measurement

There are two general methods which may be used in measuring respiration. Seeds may be continuously aerated with carbon dioxide-free air of a relative humidity which will not produce a change in the moisture content of the seeds during the measurement. Air withdrawn from the respiration chambers maintained under these conditions can then be analyzed for its carbon dioxide and oxygen content. Examples of types of apparatus adapted to this method are those developed by Bailey,[14] Ramstad and Geddes,[39] and Milner,[41] for measurement of the respiration of cereal grain, flaxseed, and soybeans.

An alternative procedure is to maintain the seeds in a closed container for an interval of time sufficiently long to permit a detectable change in the atmosphere in the container, after which a sample of this air is withdrawn and analyzed. Since a large accumulation of carbon dioxide in the atmosphere surrounding the seeds inhibits respiration,[39] a period of storage must be employed which will not permit the development of more than about 3% carbon dioxide. Harrington and Crocker[46] employed such a method for the measurement of the respiration of many types of plant materials, and Malowan,[38] as well as Altschul *et al.*,[47] investigated cottonseed respiration by such a procedure.

D. Respiratory Quotient

The ratio of the volume of carbon dioxide evolved to that of oxygen absorbed during the respiration is termed the *respiratory quotient* or RQ.

[46] G. T. Harrington and W. Crocker, *J. Agr. Research*, **23,** 101–115 (1923).
[47] A. M. Altschul, M. L. Karon, and P. J. Fynn, *Plant Physiol.*, **21,** 410–415 (1946).

It has been assumed that this quotient is strictly dependent upon the type of foodstuff that is supporting the respiration. Thus, if carbohydrates are consumed, the RQ should be unity according to the equation:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$$

If organic acids, rich in oxygen, are consumed, the RQ will be greater than unity, *e.g.*, 1.6 for tartaric acid and 4 for oxalic acid. On the other hand, if fats or proteins are consumed, the RQ will be less than unity, *e.g.*, 0.7 for fats and 0.8 for proteins.

However, factors other than the nature of the material consumed affect the respiratory quotient. Among these are temperature, aerobic fermentation, and carbon dioxide assimilation. Harrington [48] found that the RQ of dormant apple seeds increases with increasing temperature of storage. The respiratory quotient by itself, therefore, cannot furnish precise information concerning the respiratory process. Only in connection with other observations can it be of value. Also, as clearly pointed out by Harrington,[48] "neither oxygen consumption nor carbon dioxide evolution can be considered an accurate index of respiratory activity. Both depend on external and internal conditions which affect the two differently, so that neither alone gives a complete picture, much less a satisfactory understanding of respiratory exchanges." The use by many investigators of data relative to carbon dioxide evolution as the sole measure of respiration involves an assumption that must be experimentally justified.

Karon and Altschul [49] measured the respiratory quotient of 17 samples of resting cottonseed and concluded that its value is unity. As pointed out in the proceeding section, there is a considerable decrease in the total sugar content of cottonseed during heating, but no decrease in total oil content. Such evidence supports and supplements the results of respiration investigations and renders it almost certain that carbohydrates are the principle materials involved in the respiration of cottonseed. Ramstad and Geddes [39] concluded on the basis of changes occurring in the concentration of sugar during the storage of soybeans and specific heat measurements that carbohydrates are the first food materials utilized in the respiration of soybeans. Milner [41] found that in the temperature range of 25–40° C. the RQ of high-moisture soybeans is practically unity.

E. Quantitative Representation

Karon and Altschul [49] measured the respiration of several varieties of cottonseed as a function of their moisture content, age, and maturity. Typical results on the effect of moisture content and length of storage are given in Figure 31. In this figure the best smooth curves are drawn

[48] G. T. Harrington, *J. Agr. Research*, **23**, 117–130 (1923).
[49] M. L. Karon and A. M. Altschul, *Plant Physiol.*, **21**, 506–521 (1946).

from the experimental data. Each horizontal bar represents a complete respiration measurement; the height of the bar above the horizontal axis is equal to the average rate of respiration for the period during which the seeds were maintained in the respiration flask, and the length of the bar

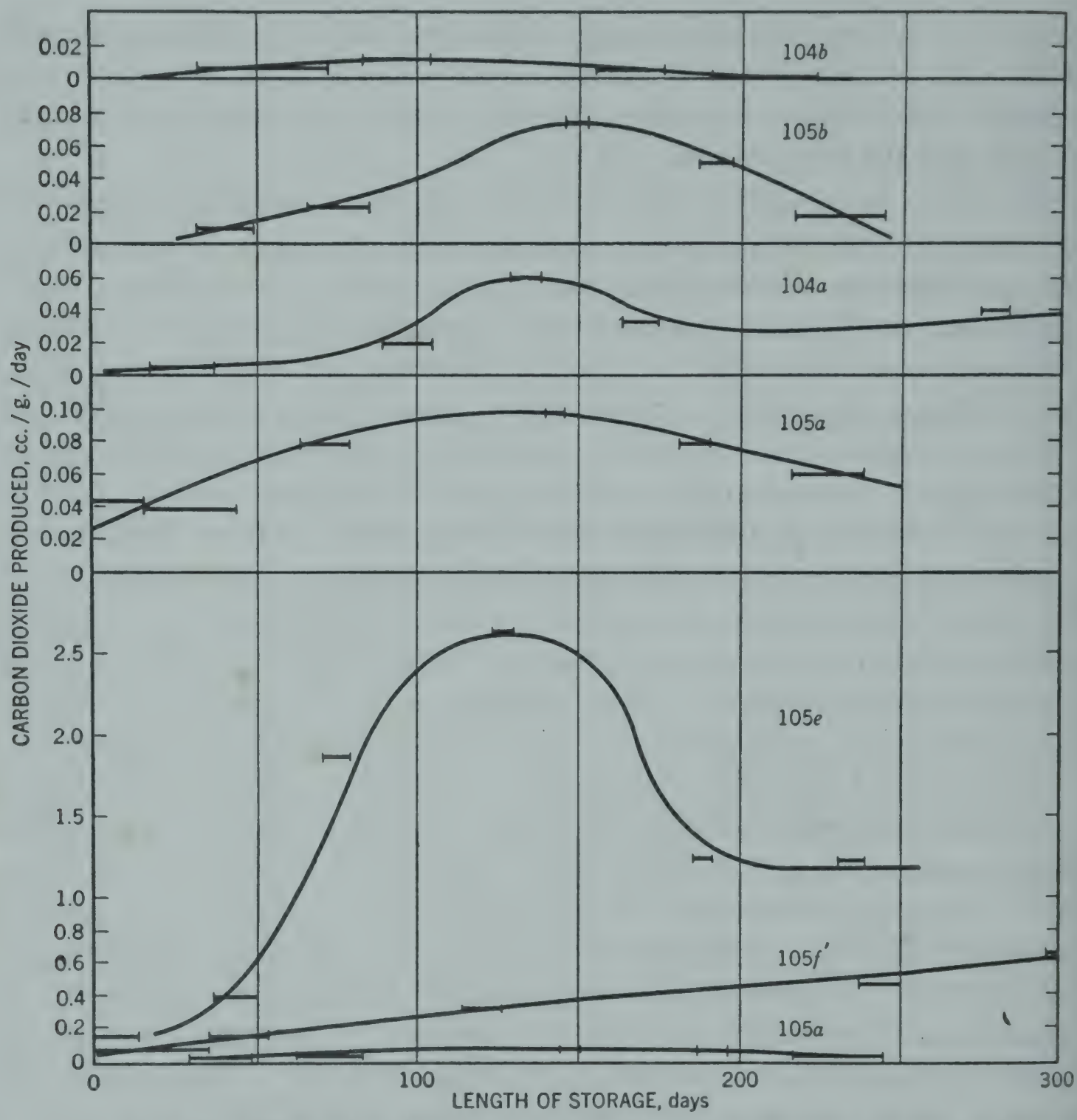


Fig. 31. Effect of moisture content and length of storage on respiration of Delfos variety cottonseed.[49]

Sample no.	Moisture content (wet basis), %	Sample no.	Moisture content (wet basis), %
104*b*	10.0	105*a*	13.1
105*b*	10.7	105*f'*	14.9
104*a*	12.0	105*e*	16.8

is equal to the time interval of the experiment. In order to present on one graph the respiration curves for all the samples, the ordinate scale for each sample has been adjusted to the intensity of the respiration.

It can readily be seen from an examination of this figure that the intensity of respiration of any given sample depends on the length of

time that it has been stored. The choice of any given interval for measurement of respiration is arbitrary and does not provide an adequate evaluation of the over-all process from the time that the seeds were received until they were milled or planted. Yet such a procedure has been generally used by investigators of the respiration of plant materials. Thus, respiration intensity has been generally defined as the rate of production of carbon dioxide or consumption of oxygen by a fixed weight of seeds for a stated time interval from the time they were received in the laboratory or from the time that they were conditioned to the desired moisture content. This interval may vary from a few days to years depending upon the convenience of the investigator and objectives being sought.

In order to obviate this objection and to provide a more representative expression of respiration, Karon and Altschul applied a method of averaging and defined "average respiration intensity," *RI*. Evaluation of *RI* from data such as given in Figure 31 was made by integration of the area under the respiratory patterns, and division of the total number of cubic centimeters of carbon dioxide evolved by the total time in days of the experiment. In spite of its empirical nature, this value of "average respiration intensity," because it covers a longer interval of storage, probably approaches more closely than any other value to a "true" respiration intensity of resting seeds.

F. Effect of Moisture

The respiration of cottonseed increases with increasing moisture content [9, 38, 49] when the moisture content is the sole variable (*i.e.*, when samples from one lot of seeds are conditioned to various moisture contents and stored at the same temperature). The rise in respiration is a regular function of the moisture content and is subject to mathematical analysis. In Figure 32 is shown the effect of moisture on the average respiratory intensity of cottonseed.[49] Although only carbon dioxide evolution is reported, the authors also measured the oxygen absorption on the same samples and found that the respiratory quotient was unity. Three different cottonseed varieties are represented in Figure 32; in each case a plot of the data yielded a smooth curve. These 3 curves correspond to the simple exponential relationship, $y = ae^{bx}$,

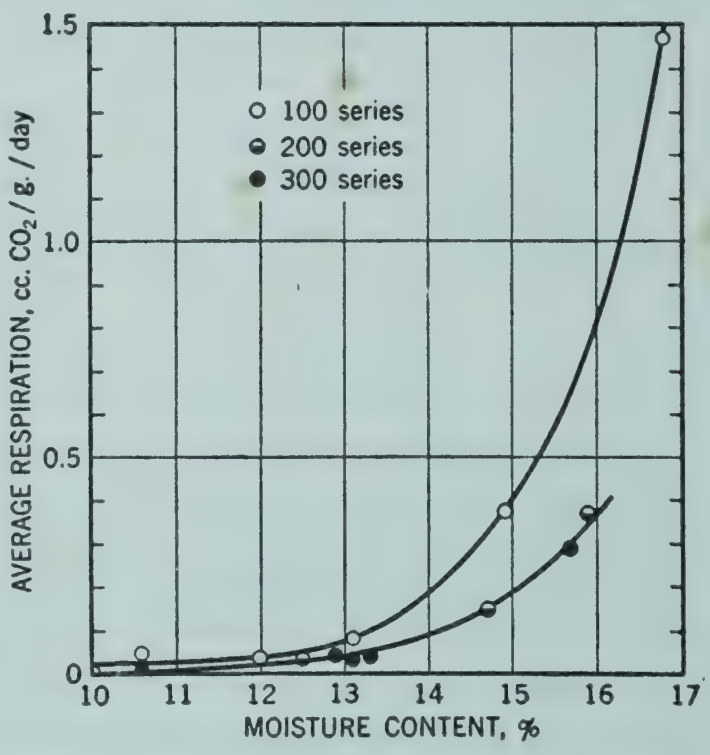


Fig. 32. Effect of moisture (wet basis) on average respiratory intensity of cottonseed: 100 series, Delfos variety; 200 series, Coker's variety; 300 series, Oklahoma Triumph variety.[49]

where y is the average respiratory intensity, x is the moisture content (wet basis), and a and b are constants characteristic of the material investigated. A plot of log y against x for the data in Figure 32 gives straight lines with a slope equal to 0.35 log unit per 1% increase in moisture content.[49] The only difference between the Delfos variety (100 series, Fig. 32) and the Coker's and Oklahoma Triumph varieties (200 and 300 series) is that the line representing the latter two series is displaced 1% on the moisture axis.

Some idea of the range of respiration of cottonseed may also be observed in Figure 32. The Delfos variety had an average respiration intensity of 0.38 cc. of carbon dioxide per g. of dry seeds per day at the 15% moisture level, whereas the *RI* value under the same conditions for

TABLE 47

Comparison of Respiration of Cottonseed, Flaxseed, and Sunflower Seed

Type of seed	Moisture content (wet basis), %	Average respiration intensity, *RI*, cc. CO_2 per g. per day
Cottonseed, Delfos variety	13.1	0.076
Cottonseed, Coker's variety	12.5	0.027
Cottonseed, Oklahoma Triumph variety	13.3	0.051
Flaxseed	12.8	0.023
	13.7	0.064
	16.5	0.19
Sunflower seed	11.8	0.039
	13.2	0.073
	14.0	0.15

each of the other two varieties was 0.17. Malowan [38] obtained a value of 0.091 for the respiration of a sample of cottonseed with a moisture content of 15.9% (wet basis) and Franco [9] obtained the low value of 0.019 for seed with a 15% moisture content. Inasmuch as the intervals for the respiration measurement used by each of the above investigators differed, it is not possible to compare their results directly. These results again emphasize the desireability of reporting biological measurements in a uniform manner.

Larmour *et al.*[50] measured the respiration of flaxseed and sunflower seed at various moisture contents. Their data were analyzed by Karon and Altschul [49] to obtain average respiration intensity values which are compared with those for cottonseed in Table 47. It was concluded from this comparison that cottonseed, flaxseed, and sunflower seed of equivalent moisture contents respire at approximately the same level of intensity.

[50] R. K. Larmour, H. R. Sallans, and B. M. Craig, *Can. J. Research,* **F22,** 9–18 (1944).

On the basis of a general study of the effect of moisture on the respiration of cereal grains and flaxseed, Bailey [14] concluded that flaxseed has a higher respiration intensity at equivalent moisture contents than have cereal grains. He suggested that the difference may be due to the fact that in flaxseed the moisture is distributed only in the hydrophilic portion of the seed. Thus, on the basis of a 40% oil content (dry basis), a moisture content of 10% for the entire seed would correspond to an actual content of water in the hydrophilic portion of approximately 16.5%. The fact that flaxseed, sunflower seed, and cottonseed have respiration intensities of the same order of magnitude seems to suggest that all oilseeds respire at a higher intensity than do cereal grains.

G. Immature Seeds

Immature seeds apparently respire at a higher level of intensity than mature seeds of equal moisture content.[49] A sample of Coker's variety of cottonseed containing 12.5% moisture (wet basis), obtained from bolls prematurely cracked open, had an average respiration intensity of 0.14 cc. of carbon dioxide per g. per day. Another sample of seeds of the same variety, grown at the same location, and harvested on the same day, but from bolls which had properly matured, had a respiration intensity of 0.027 at the same moisture content.

H. Effect of Temperature and Atmosphere

Respiration is increased at higher temperatures as is shown in Table 48. The respiration of cottonseed is greatly inhibited through the removal

TABLE 48

Effect of Temperature on the Respiration of Cottonseed[a]

Room temperature			Temperature, 120°F.		
Moisture content, %	Treatment	Respiration[b]	Moisture content, %	Treatment	Respiration[b]
9.0	None	39.4	8.7	None	76.7
15.9	Wetted	138.2	16.2	Wetted	493.9
23.2	Wetted	705.2	22.9	Wetted	937.1
28.7	Wetted	1127.5	29.2	Wetted	1770.5

[a] J. Malowan, *Cotton Oil Press*, **4**, No. 11, 47–49 (1921).
[b] Milligrams of carbon dioxide generated in six days by 150 g. of seeds.

of oxygen from the atmosphere surrounding the seeds. Malowan [38] compared the respiration of cottonseed in atmospheres of hydrogen and oxygen. In one experiment, 150-g. lots of seed with a moisture content of 21% (wet basis) were kept in respiration flasks for one week. The seeds in the flask containing hydrogen evolved 72.7 mg. of carbon dioxide, compared to 1,044.6 mg. evolved from the seeds in the flask containing oxygen.

VIII. Lipolysis

It has been mentioned previously that lipolysis (hydrolysis of glycerides to form free fatty acids) takes place upon germination and during heating. This activity, however, is dependent on neither germination nor heating and can take place at normal temperatures in seeds with moisture contents lower than that required for germination.

A. Methods of Measurement and Quantitative Representation

Free fatty acids may be determined in the entire seed [45] or on the oil extracted from the seeds by means of suitable solvents.[51] The latter method is preferable because it is more accurate and yields results comparable with those observed when the seed is processed.

Typical curves relating the effect of the moisture content on the rate of formation of free fatty acids in cottonseed are given in Figure 33. Examination of these curves reveals the fact that the rate of lipolysis is

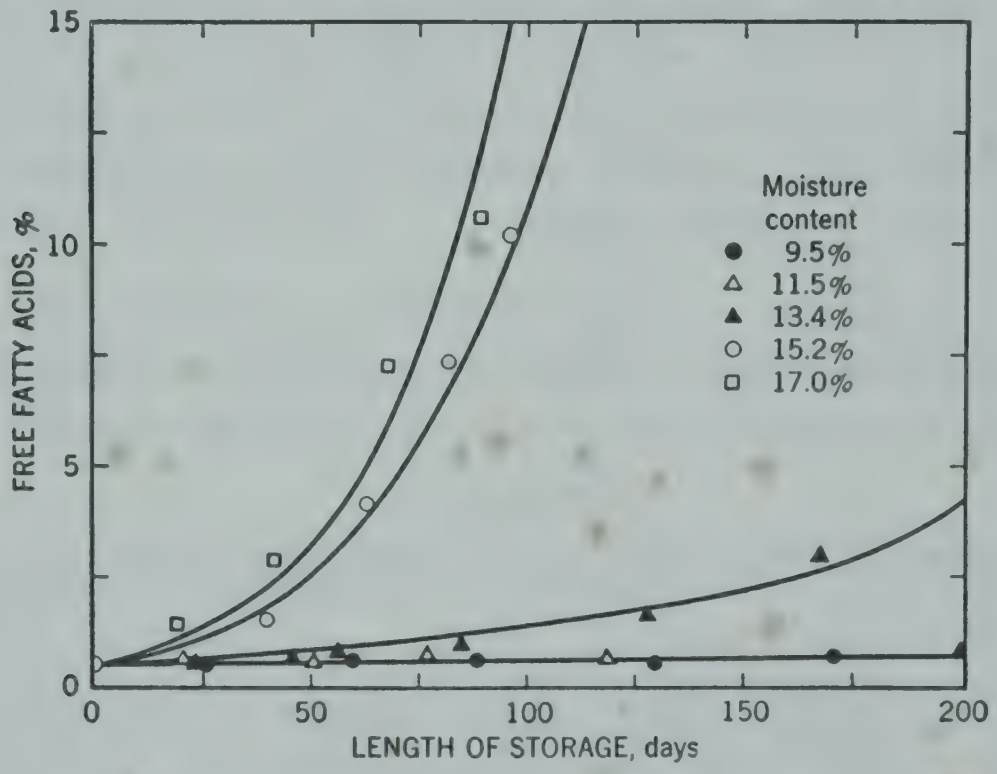


Fig. 33. Pattern of lipolysis in cottonseed.[31]

not uniform, but increases as the storage proceeds. More free fatty acids are generally formed in the second of two successive and equal storage periods. Such behavior is indicative of an autocatalytic type of reaction and the curves should be amenable to mathematical analysis. Karon and Altschul [31] found that the differential equation:

$$dF/dt = kF\ (100 - F)$$

characterizes the curves of the type given in Figure 33. In this equation, F is the percentage of free fatty acids formed, $100 - F$ is the percentage of residual unhydrolyzed fat, t is the length of storage, and k is the rate

[51] American Oil Chemists' Society, Official and Tentative Methods, 1941.

constant characteristic of the lipolysis. The value of k is determined by plotting $\log \frac{F}{100 - F}$ against the length of storage, t, to yield a straight line with a slope equal to $\frac{100k}{2.3}$. Once the value of k is determined, it is possible to reconstruct the lipolysis curve for the sample and, within reasonable limits, to predict the percentage of free fatty acids that will be developed if the storage is continued for any given time. The principal value of the rate constant lies in the fact that it permits simple and quantitative evaluation of the effect of moisture or other variables on the rate of lipolysis and makes possible the comparison of lipolysis with other biological activities.

B. Effect of Moisture

Freyer,[52] Olcott and Fontaine,[53] and Robertson and Campbell[54] pointed out that increase in moisture in cottonseed is accompanied by an

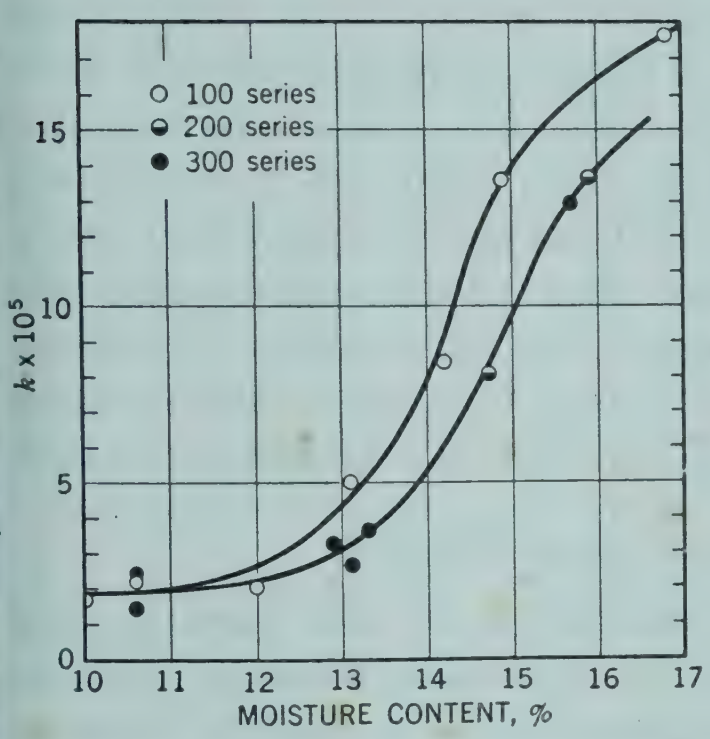


Fig. 34. Effect of moisture (wet basis) on lipolysis rate constant for cottonseed: 100 series, Delfos variety; 200 series, Coker's variety; 300 series, Oklahoma Triumph variety.[55]

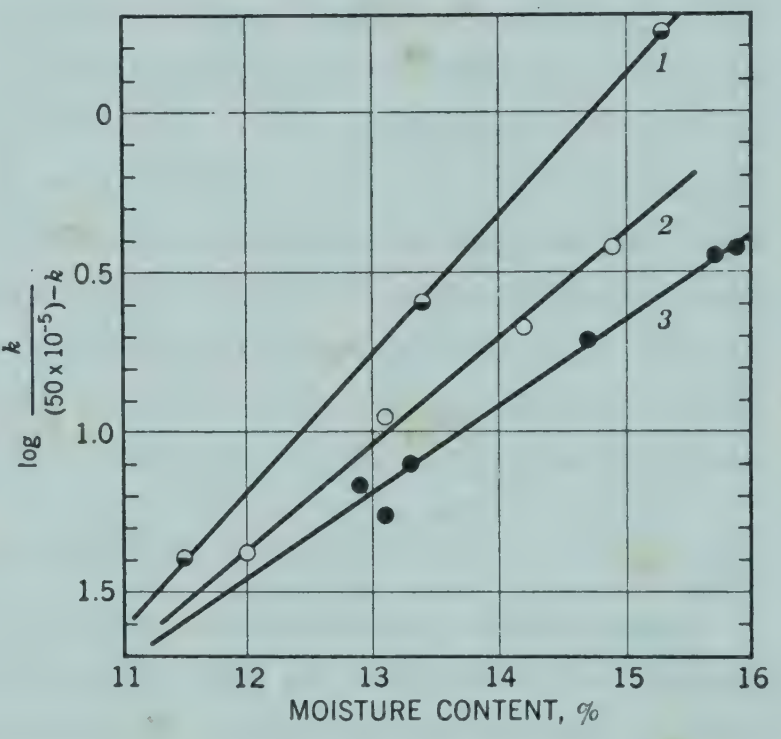


Fig. 35. Effect of moisture content of cottonseed as a function of the lipolysis rate constant: curve *1*, Delfos harvested 1941[31]; *2*, Delfos, 1942[55]; *3*, Coker's and Oklahoma Triumph, 1942.[55]

increased rate of lipolysis. Karon and Altschul,[31] and Kyame and Altschul[55] (*cf.* also Karon[56] and Kyame[57]) investigated the effect on the rate of lipolysis at 25° C. of artificially conditioning cottonseed to

[52] E. Freyer, *Oil & Soap,* **11,** 162–164, 176 (1934).
[53] H. S. Olcott and T. D. Fontaine, *Oil & Soap,* **18,** 123–124 (1941).
[54] F. R. Robertson and J. G. Campbell, *Oil & Soap,* **10,** 146–147 (1933).
[55] L. Kyame and A. M. Altschul, *Plant Physiol.,* **21,** 550–561 (1946).
[56] M. L. Karon, *Master's Dissertation,* University of Minnesota, 1942.
[57] L. Kyame, *Master's Dissertation,* Tulane University, 1943.

different moisture contents. Rate constants for three different varieties of seeds harvested at different times during the season and conditioned to a wide range of moistures are given in Figure 34. The samples referred to in Figure 34 are the same as those employed in the respiration investigations [49] which were discussed on page 185. It is of interest to note that the lipolysis rate constant increases in a regular manner with increase in moisture content of the seed, and that seeds which exhibit a high respiratory intensity also have a high intensity of lipolysis.

Kyame and Altschul [55] found a linear relationship between moisture content and lipolysis similar to that which was observed between moisture content and respiration. The differential equation relating lipolysis to moisture content is:

$$dk/dm = k'k\ (A - k)$$

where k = lipolysis rate constant, m = percentage of moisture in the seeds, k' = constant relating moisture to lipolysis, and A = a constant. This equation has been applied to an analysis of the curves in Figure 34 as well as of the rate constants calculated for the curves in Figure 33. With a value of A equal to 50×10^{-5}, straight lines were obtained representing the effect of moisture on lipolysis as is shown in Figure 35. It can be seen that the sample of cottonseed from the 1941 harvest of the Delfos variety had a higher rate of lipolysis than any of the other samples and also exhibited a greater sensitivity to increased moisture content. In general, it seems that seeds which have a high rate of lipolysis at low moisture contents will also exhibit a higher sensitivity to increased moisture content.

C. Effect of Temperature of Storage

Simpson [24] conducted a series of experiments on the Carolina Dell variety of cottonseed to determine the effect of combinations of temperature of storage and moisture on lipolysis. His results are given in Table 49. It can be seen from these results that optimum conditions for lipolysis comprise both a high temperature and a high moisture content. Conversely, lipolysis can be avoided, or at least minimized, by storing the seeds at a very low temperature, *i.e.*, near freezing.

D. Effect of Application of Heat

In connection with their investigations on drying seed cotton at elevated temperatures to facilitate ginning, Rusca and Gerdes [30] noted the effect of temperature on the rate of lipolysis. Although their procedure was effective in reducing the moisture in the lint, it had little effect on the moisture content of the seed; nevertheless, they observed a pronounced lowering of lipolysis as is shown in Table 50. Robertson and Campbell [54] obtained similar results in heating moist seeds to 175° F. before storing.

When, however, they heated dry seeds to 175° F. for eight hours and then followed this treatment by storage for two weeks in a moist atmosphere, they found that the preheating accelerated lipolysis.

TABLE 49

Effect of Temperature and Moisture on Free Fatty Acid Content of Cottonseed after Two Years' Storage[a]

Moisture content (wet basis), %	Temperature, °F.			
	90	Air[b]	70	33
	Free fatty acid content, %			
7.1	0.9	0.5	0.7	0.4
8.8	1.7	0.9	0.8	0.4
10.6	2.7	1.3	1.0	0.7
12.6	10.0	2.6	1.8	0.6
14.7	21.9	7.4	3.0	1.0

[a] D. M. Simpson, *J. Agr. Research*, **64**, 407–419 (1942).
[b] Atmospheric temperature.

TABLE 50

Effect of Heat Drying Seed Cotton on Moisture Content and Free Fatty Acids in Seeds[a]

Condition of seed cotton	Moisture content of seeds (wet basis), %		Free fatty acid content, %	
	At gin	After 90 days	At gin	After 90 days
Undried	15.7	14.5	1.0	19.3
Dried at 160°F.	15.1	14.3	1.0	17.6
Dried at 190°F.	15.3	14.1	1.0	16.0
Dried at 220°F.	15.0	14.1	1.0	12.3

[a] R. A. Rusca and F. J. Gerdes, *U.S. Dept. Agr. Circ.*, **651** (1942).

Application of heat to seeds in order to arrest lipolytic activity is predicated on the theory that the enzyme systems can be inactivated in this manner. It must be remembered, however, that in the process of increasing the temperature, conditions favorable to lipolysis and other disintegrative activities are created. Unless the treatment is rapid and completely effective, the seeds may be left in a condition more favorable for increased than for lowered biological activity. This accounts for the inconsistent and unpredictable effects of heat treatment and heat drying which may and have been observed.

E. Effect of Immaturity

In an investigation [49, 55] of the respiration and storage of cottonseed, seeds were obtained from unopened bolls. These seeds were probably immature or perhaps field-damaged as well as immature (*cf.* Sections X and XI of this chapter), and had an exceedingly high respiration intensity. The course of lipolysis differed materially from that occurring in normal seeds with respect to both rate and pattern. Whereas normal seeds exhibit an accelerated rate of lipolysis as the length of storage progresses, the immature seeds exhibited the highest rate of lipolysis at the beginning of the storage period. As may be seen by comparing the curves in Figure 36 for the development of free fatty acids in immature and in normal seeds, the rate of lipolysis in the immature seeds at the end of 200 days of storage had decreased to practically zero, whereas in the normal seeds appreciable lipolysis was just beginning.

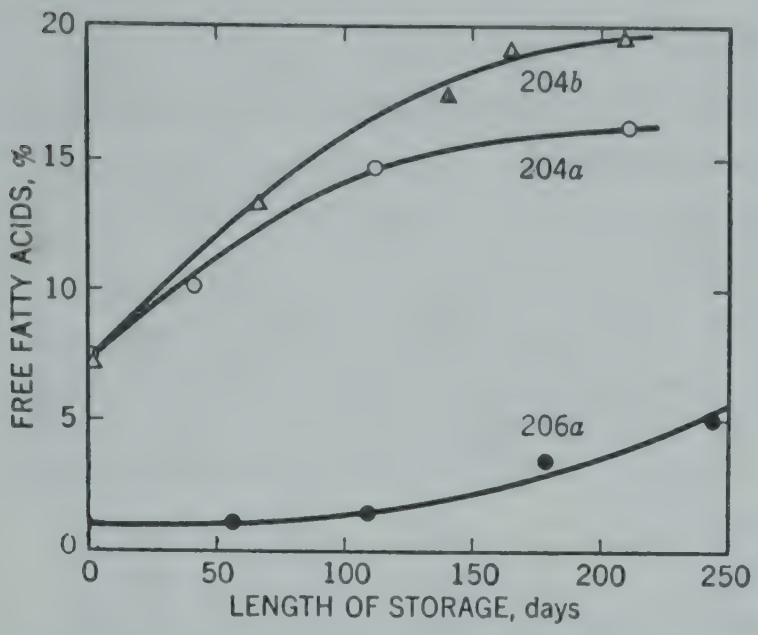


Fig. 36. Effect of immaturity on lipolysis pattern of seed (Coker's variety).[55]

Sample no.	Condition	Moisture (wet basis), %
204*a*	Immature	13.7
204*b*	Immature	12.5
206*a*	Normal	14.7

F. Effect of Disintegration

Lipolysis is facilitated by mechanical disintegration of the seeds. Ground cottonseed meats have a lipolysis rate constant, k, of 200×10^{-5} at 16% moisture (wet basis), compared to a k of 17.6×10^{-5} for whole cottonseed containing 16.8% moisture. At 13% moisture ground meats exhibit a k value of 170×10^{-5}, compared to a k of 2.6×10^{-5} to 5×10^{-5} for whole seed of the same moisture content. Flaked meats are not as highly disintegrated as ground meats and consequently do not manifest as much lipolytic activity. "Whole" kernels are intact except for superficial breaking of the outermost cells and therefore undergo lipolysis less readily than flakes but more readily than whole seed. Kernels with a moisture content of 11.9% have a k of 25×10^{-5} compared to a k of 2×10^{-5} for whole cottonseed of the same water content. A comparison of the relative rates of free fatty acid formation as a function of the degree of organization of the seed is evident from the data in Table 51.

IX. Inhibition of Biological Activity by Chemical Agents

There are numerous references in the literature to attempts to inhibit biological activity in seeds and related products by means of chemical

agents. Procopio [58] reported the effect of the action of sulfur dioxide on fresh green fodder. In concentrations of 0.8 to 1.0%, all biological and enzymatic processes were completely inhibited, and they were markedly reduced by treatment with 0.25 to 0.3% of sulfur dioxide. Hale *et al.*,[59] treated wheat containing 17% moisture with ethylene in a concentration of approximately 3 parts ethylene to 11,000 parts of air. The immediate effect of the treatment was to stimulate heating, but after storage for 200 hours the temperature of the treated seed was equal to that of the control and thereafter the treated seed required less turning to control deterioration than was required by the untreated seed. Larmour *et al.*,[60] inhibited the heating of wheat of 25% moisture content by the application

TABLE 51

Comparison of Lipolysis in Cottonseed and Cottonseed Fragments

Sample	Moisture content (wet basis), %	Length of storage, days	Free fatty acids, %
Cottonseed	16.8	90	2.7
Ground cottonseed meats	16.0	11	9.7
Cottonseed	12.0	218	0.4
Cottonseed kernels	11.9	17	0.6
Ground cottonseed meats	11.7	14	7.6
Ground cottonseed meats	8.5	35	3.4
Cottonseed flakes	9.1	33	1.1

of carbon tetrachloride. They found it necessary to supply this material continuously in order to maintain its inhibitory effects. Milner [41] observed similar results in the treatment of soybeans with this agent. Larmour *et al.*[60] were also able to inhibit carbon dioxide production in wheat by exposing it to the vapors of toluene. In so doing the embryo was permanently inactivated. Related to investigations of this type are those involving inhibition of seed germination, as exemplified by the work of Veldstra *et al.*,[61] on the physiological activity of unsaturated lactones and of Evenary *et al.*,[62] on the inhibition of germination by the application of cucumber juices.

A. Inhibition in Cottonseed

Reference has previously been made to the use of carbon dioxide [43] and hydrogen [38] as agents for inhibiting biological activity in cottonseed.

[58] M. Procopio, *Chim. ind. agr. biol.*, **18,** 240–248 (1942).
[59] W. S. Hale, S. Schwimmer, and E. G. Bayfield, *Cereal Chem.*, **20,** 224–233 (1943).
[60] R. K. Larmour, J. S. Clayton, and C. L. Wrenshall, *Can. J. Research*, **12,** 627–645 (1935).
[61] H. Veldstra and E. Havinga, *Enzymologia*, **11,** 373–380 (1946).
[62] M. Evenary, E. Konis, I. Vahl, and R. Sroelov, *Palestine J. Botany, Jerusalem Ser.*, **2,** No. 3, 1–33 (1940).

These gases were used not primarily to inhibit biological processes *per se*, but rather to reduce the concentration of oxygen which is essential for marked activity.

The first use of chemical agents as primary inhibitors for cottonseed was reported by Barrow,[13, 63, 64] who used sodium chloride to minimize heating and deterioration. The use of 5% by weight of sodium chloride for the treatment of stored cottonseed resulted in improvement in the seed and its derived products. The color of the oil was better than that produced from untreated seed of the same moisture content stored for the same length of time; the refining loss of the oil was lower than the loss from the untreated seed; the yield of oil and the feed value of the meal were unaffected; and quality of the hulls and lint were reported to be improved. It was suggested by Barrow that the action of this agent was to extract moisture from the seeds, penetrate the seed coat, and inhibit action of the enzymes and microörganisms within the seed.

TABLE 52

Effect of Chemical Inhibitors on the Respiration of Cottonseed[a]

Experiment no.	Weight of seeds, g.	Reagent	Quantity added, ml.	Final moisture content (wet basis), %	Temperature of storage, °F.	Respiration[b]
1	60	Acetic acid, 5% soln.	20	29	105	124
2	60	Ethyl alcohol, 15% soln.	20	29	105	265
3	60	Ethyl alcohol	8	—	—	—
—	—	Acetic acid	2	—	—	—
—	—	Water	15	29	105	83
4	60	Water + 18 g. starch	15	29	105	1595
5	60	Water + 10 g. cane sugar	15	29	105	1565
6	60	Water + 10 g. sodium chloride	15	29	105	76
7	100	Mercuric chloride, 10% soln.	25	29	110	1256
8	100	Sodium carbonate, 10% soln.	25	29	110	1745
9	100	Sodium chloride, 10% soln.	25	29	110	1243
10	100	Sulfuric acid, 10% soln.	25	29	110	396
11	60	Water	—	34.6	105–110	506
12	60	Formalin, 20%	—	38.9	105–110	58
13	60	Copper sulfate, 2.5% soln.	—	30.9	105–110	598
14	60	Mercuric chloride, 0.5% soln.	—	39.0	105–110	563

[a] J. Malowan, *Cotton Oil Press*, **4**, No. 11, 47–49 (1921).
[b] In experiments 1–10, respiration is expressed as milligrams CO_2 evolved per week, and in experiments 11–13, as milligrams CO_2 per three-day period.

Malowan[38] evaluated the effect of various chemicals as possible respiratory inhibitors with the results given in Table 52. In experiments 1 to 10 of this table, the seeds were artificially moistened to a moisture content of 29% (wet basis) and stored for one week at the stated temperature; in experiments 11–13, 60 g. of seeds were conditioned to the

[63] E. H. R. Barrow, U.S. Pat. 1,119,672 (1914).
[64] E. H. R. Barrow, U.S. Pat. 1,155,194 (1915).

moisture contents indicated and kept for three days at a temperature of 105–110° F. High concentrations of acetic acid, ethanol, a mixture of the two, sodium chloride, sulfuric acid, and formalin were found to inhibit respiration. Strong sodium chloride solution (12%) markedly inhibited respiration, whereas a concentration of approximately 2.5% had little effect. Because disinfecting solutions did not prevent the evolution of carbon dioxide, Malowan assumed that microörganisms are not responsible for respiration in stored cottonseed.

Karon and Altschul [31, 65] found that treatment of cottonseed with acid or alkali of sufficient concentration to materially change the *p*H of the seeds reduced the rate of lipolysis. The *p*H of normal seeds ranges from 6.5 to 7.0. When the *p*H was raised by means of ammonia to a value of about 8 or lowered with hydrogen chloride gas to 4.6, the formation of

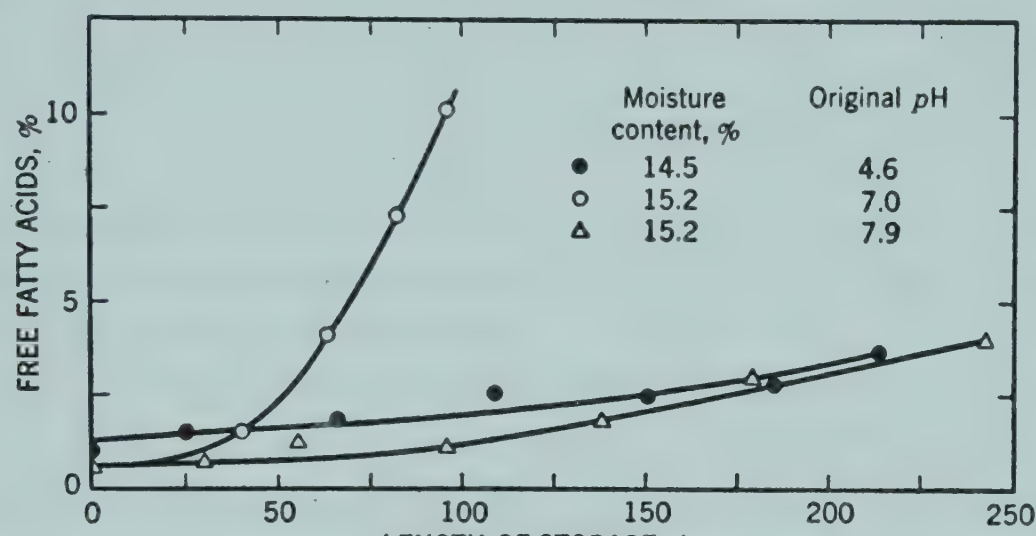


Fig. 37. Effect of acid and alkali on lipolysis in cottonseed.[31]

free fatty acids was definitely inhibited as is shown in Figure 37. Treatment of one-ton lots of cottonseed with ammonia was effective in inhibiting lipolysis and heating.[42] It was noted, however, that treatment with ammonia produced an initial increase in the temperature of the treated seed compared to the untreated control. In the laboratory experiments this initial production of heat was not observed because the total amount was small and it was rapidly dissipated in the type of apparatus used in the experiments. Even in one-ton lots of seed, the initial heating was barely perceptible because the heat was dissipated in a short time and the inhibitory effect of ammonia upon further heating predominated. Following the dissipation of the heat initially evolved, the ammonia-treated seeds remained at a lower temperature than did the untreated seeds.

Similar results were observed in another test involving treatment of

[65] A. M. Altschul and M. L. Karon (to Secretary of Agriculture), U.S. Pat. 2,376,852 (1945).

a ton of cottonseed with ammonia, as indicated in Figure 38. Even though there was an over-all improvement in the storage behavior of the seeds in this case, the damage which occurred during the initial heating reduced the ultimate effectiveness of the treatment. Further experience obtained by treating 30-ton lots of cottonseed with ammonia indicated that the amount of heat initially evolved was too large to make treatment by this agent feasible in large-scale storage.[66]

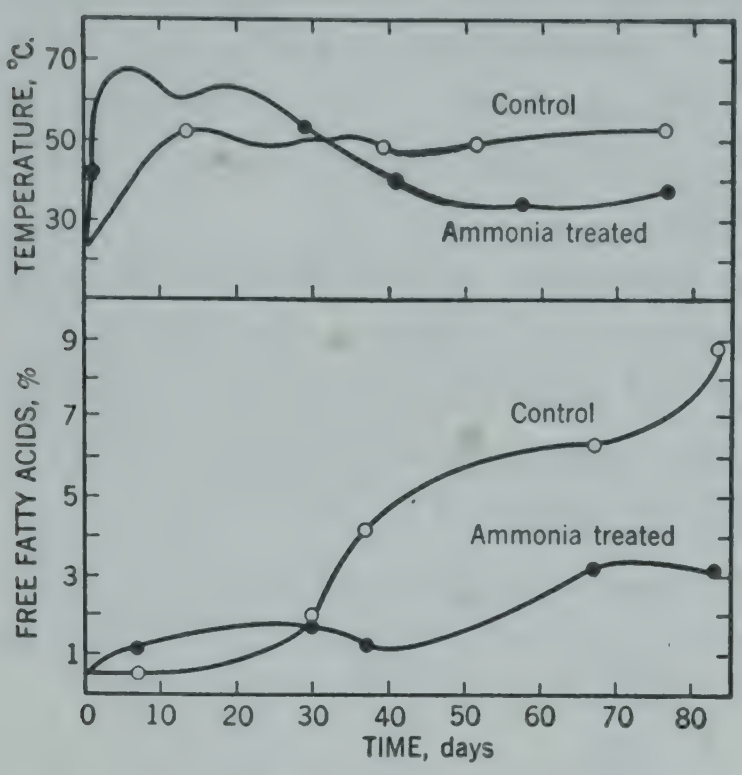


Fig. 38. Effect of ammonia treatment on heating and lipolysis in cottonseed.[43]

Altschul *et al.*,[67] investigated the effect of ammonia and several other inhibitors on both respiration and lipolysis of cottonseed with results as given in Table 53. As might be expected on the basis of the previously mentioned experiments with ammonia, both respiration and lipolysis were inhibited. An examination of the respiration pattern for cottonseed [67] revealed that treatment with ammonia resulted in an initial stimulation followed by inhibition of such magnitude that the average respiration intensity was lower than that of the untreated control. All of the other compounds referred to in Table 53 possess fungistatic activity, but when used to treat cottonseed prior to storage they stimulated respiration, and only one of them, Nacconol NR, markedly inhibited lipolysis. One might be led to conclude from these results as did Malowan, that microörganisms play an unimportant role in the biological activity in cottonseed. As will be explained later, such a conclusion is not strictly warranted.

B. Effect of Immaturity, Deterioration, and Disintegration of the Seeds

Altschul and co-workers [67] found that treatment of single lot of immature cottonseed with ammonia produced an over-all inhibition of respiration, but stimulated lipolysis.

The success which may be achieved in producing inhibition of biological activity depends to a considerable extent on the history of the material being treated, *i.e.*, on the degree to which the specified activity

[66] A. M. Altschul, M. E. Curet, M. L. Karon, C. M. Hall, and B. A. Smith, *Oil Mill Gazetteer*, **50**, No. 8, 9–13, 23 (1946).

[67] A. M. Altschul, M. L. Karon, L. Kyame, and C. M. Hall, *Plant Physiol.*, **21**, 573–587 (1946).

TABLE 53

Effect of Inhibitors on Respiration and Lipolysis of Cottonseed[a]

Inhibitor	Respiration,[b] %	Lipolysis,[b] %
Ammonia, average *p*H of 8.03	17	48
Ammonia, average *p*H of 7.91	62	71
Nacconol NR, 4.4%	169	45
Butylmaleimide, exposed to vapors	232	100
Emulsol 607, 0.1%	261	100

[a] A. M. Altschul, M. L. Karon, L. Kyame, and C. M. Hall, *Plant Physiol.*, **21**, 573–587 (1946).

[b] Percentage in terms of normal respiration and lipolysis.

has already developed in the material. Altschul [68] pointed out that the inhibition of lipolysis obtained by treating cottonseed with ammonia was greater with seeds which had not begun to deteriorate. For example, in one experiment a lot of seeds having a moisture content of 16.7% was stored for 111 days, during which the free fatty acid content rose to 5.3%. At this stage, one portion of the sample was treated with ammonia. After additional storage of thirty-six days, the ammonia-treated portion of the seeds contained 11.4% free fatty acids compared to 13.9% in the untreated portion.

In experiments involving lipolysis in ground meats, it was found that ammonia, in concentrations which were effective on intact cottonseed, had less inhibitory effect on the ground meats. Ammonia-treated meats having a moisture content of 17% developed 14.5% free fatty acids compared to 55% in the meats of an untreated control.

C. General Nature of Chemical Inhibition

The inhibition of biological activity in cottonseed or in any other type of seed does not differ fundamentally from the same phenomenon as it occurs in other types of living material, plant or animal. Consequently, much may be learned from the application of the generally available knowledge in this field to the specific problem of the cottonseed.

It has been pointed out that there is an initial stimulation of both heating and respiration following treatment of cottonseed with ammonia. As indicated by the data in Table 53 treatment of cottonseed with Nacconol NR, Emulsol, or butylmaleimide caused a stimulation of respiration. The last two substances had no effect on lipolysis, while the first produced marked inhibition of lipolysis. These observations are typical of the mode of action of chemical agents on living systems and

[68] A. M. Altschul, *Oil Mill Gazetteer*, **49**, No. 1, 8, 13 (1944).

are clearly illustrated in the work of Irving [69] on the effect of chloroform vapors on the respiration of leaves. Figure 39 reproduces her diagrammatic representation of the effect of increasing quantities of chloroform on leaf respiration. When a very small quantity of chloroform was used, only stimulation of respiration was observed (Curve *A*). As the quantity of chloroform was increased, the intensity of stimulation was increased but the duration of stimulation decreased. A somewhat larger quantity of chloroform (Curve *B*) still failed to produce inhibition. With a still greater quantity of chloroform (Curve *C*), an initial stimulation occurred, followed by marked inhibition. When an extremely large quantity of chloroform was used (Curve *E*), no initial stimulation was evident. It is interesting to note that, when intermediate quantities of chloroform were used, there was a tendency for the respiration to increase again—following dissipation of the effects of the reagent. These results illustrate the fact that the same chemical may act either as a stimulant or as an inhibitor, depending upon its concentration; in low concentrations it may act as a stimulator of biological activity and in higher concentrations as an inhibitor of the same activity.

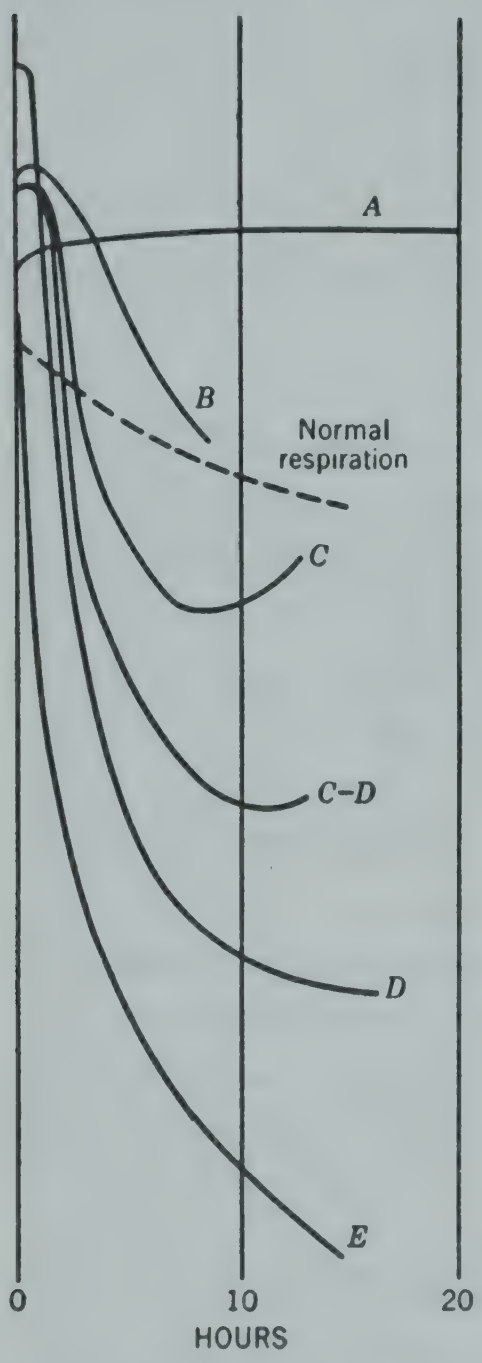


Fig. 39. Effect of chloroform on leaf respiration.[69] *A* represents lowest and *E* highest concentration of chloroform.

In the course of any given treatment, the concentration of the chemical in a particular tissue may successively pass through a stimulating, inhibiting, and again a stimulating stage. This sequence of effects apparently occurred in the case of the leaf experiment illustrated in Curve *C* of Figure 39 and generally occurs when cottonseed is treated with ammonia. As ammonia penetrates into the seed, it is present first in a small concentration which serves to stimulate respiration and heating. With increasing penetration into the tissue, a concentration is ultimately reached which produces inhibition. If the seeds in the latter condition are subjected to aeration to remove the ammonia, the process may be reversed and the concentration of the ammonia may be reduced to such a low value that stimulation of the biological activity takes place.

Because of this relationship between concentration of the chemical applied and biological activity, it must be concluded that chemical stimu-

[69] A. A. Irving, *Ann. Botany*, **25**, 1077–1099 (1911).

lation of biological activity can only be avoided if the chemical is able to penetrate with sufficient rapidity into the tissues to quickly build up to an inhibitory concentration. The cottonseed-ammonia system does not conform to these requirements.

It is also evident that in order to maintain inhibition for any length of time it is necessary to use a chemical which will remain in the tissue in the required concentration throughout the desired interval. The use of insufficient quantities of inhibitor will not only fail to produce and maintain inhibition, but may serve to produce stimulation of the biological activity which it is desired to inhibit.

The fact that the concentraton of Nacconol NR used in the experiment recorded in Table 53 was sufficient to inhibit lipolysis but was in the stimulatory range with respect to respiration demonstrates that the relationship between concentration of a given chemical and type of resulting activity may vary with each biological activity. The fact that the use of a given chemical in a specified concentration will inhibit lipolysis does not warrant any assumptons concerning the effect that the same chemical in the same concentration will exert on other biological processes in the same seed.

The relation between inhibition and the factors of immaturity, and degree of deterioration and disintegration of the seed demonstrates another general characteristic of biological processes which has been commented on by Altschul.[68] In order to inhibit lipolysis, for example, it is not necessary to inhibit directly the lipolytic enzymes of the seed. The chain of events from the initiation of conditions suitable for biological activity to the actual onset of lipolysis may involve many activities and many intermediate enzyme systems. Inhibition of any enzyme participating in this chain will prevent the occurrence of the final process. For this reason biological activity is more readily inhibited in a completely integrated seed than in one in which the integration has never been completely achieved or has been disturbed. As soon as the organization of the seed is destroyed, the number of pathways of biological processes is multiplied. Inhibition then becomes increasingly difficult to achieve and ultimately requires that the specific enzyme system responsible for the activity (*e.g.*, lipases in the case of lipolysis) be acted upon directly.

X. Deterioration

In the preceding sections, biological activity has been discussed in terms of specific chemical or physical reactions. From the point of view of the cottonseed industry these activities become of economic importance when they combine to produce a reduction in the quality or quantity of the seed products or destruction of viability of the seed. In the remaining

sections of this chapter, biological activity will be discussed with respect to its more general and practical significance.

A. Types of Deterioration

Two types of deterioration are recognized by the industry, namely, field damage and storage damage. As their designations indicate, field damage refers to that type of deterioration which occurs while the seeds are still in the cotton boll in the field, while storage damage refers to deterioration which occurs after the cotton has been ginned and the seeds are stored at the gin or the oil mill.

The two types of damage may be distinguished by the appearance of the seeds and by the color of the oil produced therefrom. Field-damaged seeds may have a prime color, whereas storage-damaged seeds are invariably discolored.[70] Both types yield oil having a higher content of free fatty acids than do prime seeds. Other things being equal, field-damaged seed do not yield oil as discolored as that from storage-damaged seed.

Experienced oil mill operators can readily detect the difference between these two types of damage, and can even arrive at a fairly good estimate of the free fatty acid content and quality of the oil by observation of the background color and color of the pigment glands in cross sections of the seeds. Prime seed are characterized by a creamy white background color. Fresh, prime seed contain very lightly pigmented glands and, as the seed increase in age, the color in the pigment glands becomes more intense.

Field-damaged seed have a greenish background color or, in cases of extensive damage, a greenish-brown color. Additional information concerning the age of the seed and extent of damage may be gained by examination of the pigment glands. Storage-damaged seed are characterized by a background color ranging from light brown to almost black.

B. Field Damage

The nature and causes of field damage are not easily ascertained because of the difficulties involved in conducting controlled experiments. For this reason most of the information on this type of damage is derived from reports of mill receipts.

O'Kelly and Hull [71] reported the results of systematic investigations of the relation between time of harvesting and the content of free fatty acid of cottonseeds. Large plots of cotton were employed in these experiments and successive harvestings of cotton from the same plot were made at two- to three-week intervals after the beginning of the 1933 cotton harvest. The percentages of free fatty acids corresponding to 6 successive

[70] J. Malowan, *Oil & Fat Ind.*, **4**, 127–130 (1927).
[71] J. F. O'Kelly and W. W. Hull, *Mississippi Agr. Expt. Sta. Bull.*, **316** (1936).

harvesting were in the case of Variety A: 0.62, 0.46, 0.71, 1.10, 1.85, and 3.27, respectively, and with Variety B: 0.86, 0.98, 1.05, 1.54, 1.84, and 2.93, respectively.

Field damage is pronounced in harvest seasons in which there is excessive rainfall, as is illustrated in Figure 40 where field damage is measured in terms of its effect on viability. In the 1933 season, when there was very little rainfall, the percentage of damaged seeds (seeds which

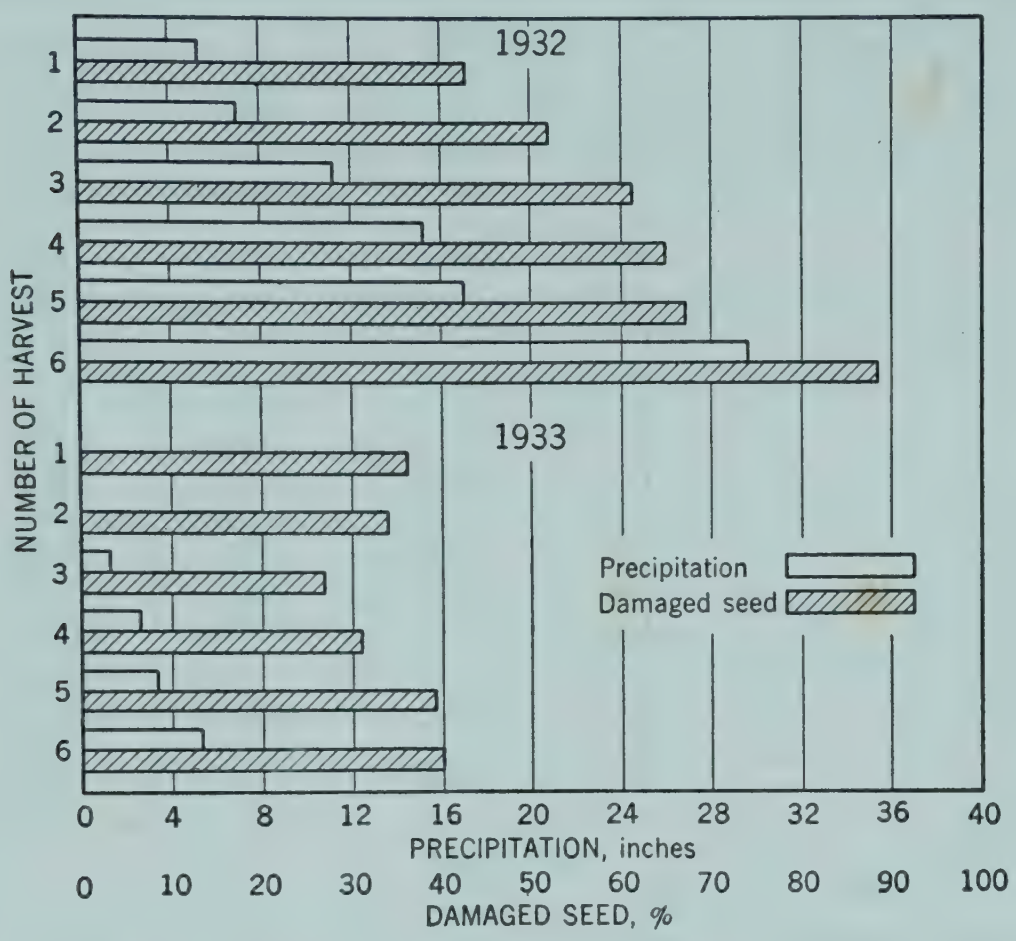


Fig. 40. Effect of delayed harvest on field damage.[71]

failed to germinate) remained fairly constant for 6 successive harvestings, whereas in 1932, when the amount of rainfall was much greater, the extent of damage increased with each successive harvesting.

An examination of the reports of the Barrow-Agee Laboratories[72] makes possible a broader evaluation of the effect of the time of harvest on the free fatty acid content of cottonseed. These reports represent the results of the analyses of cottonseed received at oil mills in the form of monthly averages by states. Although in some instances there may have been some delay between the receipt of the seed cotton at the gins and the delivery of the seeds to the oil mills, any observed damage may generally be attributed to field damage.

Average results for the 1944–45 and 1945–46 seasons are given in Table 54. These figures demonstrate the lack of correlation between free fatty acid and moisture content in cottonseed. Seed received in Tennessee during both seasons had a higher moisture content than that received in

[72] *Barrow-Agee Reports*, Barrow-Agee Laboratories, Memphis, Tennessee.

Louisiana, yet the seeds in the latter state had a considerably higher free fatty acid content. Cottonseed from the 1945–46 crop at Mississippi mills

TABLE 54

Monthly Averages by States of Percentages of Free Fatty Acids, Moisture, and Oil in Cottonseed Received at Oil Mills, 1944–1945 and 1945–1946[a]

Month	Quantity measured	Mississippi	Arkansas	Louisiana	Tennessee
1944–1945					
September	M[b]	14.0	13.3	13.6	14.0
	F[c]	1.2	0.7	2.1	0.7
	O[d]	18.6	18.4	18.1	18.1
November	M	9.3	8.9	9.8	10.4
	F	1.6	0.6	2.4	0.6
	O	19.5	19.1	18.7	19.2
December	M	11.3	12.2	11.3	12.5
	F	2.1	0.6	2.1	0.7
	O	19.0	17.8	18.5	18.1
January	M	14.0	12.5	11.4	13.0
	F	2.4	0.7	2.6	0.9
	O	18.4	17.6	18.4	17.9
February, March	M	12.4	14.1	11.5	14.2
	F	4.7	1.4	4.9	2.0
	O	18.7	17.3	18.4	17.4
1945–1946					
August, September, October	M	12.7	15.5	13.0	16.0
	F	1.1	1.0	2.5	1.1
	O	19.4	18.3	19.5	18.3
November	M	12.0	13.5	12.2	14.1
	F	2.3	0.9	4.2	0.8
	O	19.6	18.3	19.5	18.4
December	M	12.3	13.2	11.8	14.2
	F	3.0	1.1	5.5	0.8
	O	19.4	17.7	19.6	18.1
January	M	13.2	14.9	12.4	14.1
	F	4.2	1.1	5.4	1.0
	O	19.2	16.5	19.2	17.9
February	M	13.0	13.3	12.1	13.2
	F	8.3	1.3	8.5	1.5
	O	19.0	16.3	19.1	17.7
March	M	11.6	11.8	11.2	11.5
	F	10.5	1.9	11.3	2.2
	O	19.4	16.5	19.1	17.7

[a] *Barrow-Agee Reports*, Barrow-Agee Laboratories, Memphis, Tennessee.
[b] M = per cent moisture (wet basis).
[c] F = per cent free fatty acids.
[d] O = per cent oil.

had an average moisture content of 12.5% compared to 12.2% for the preceding season, yet the seeds received at the end of March, 1946 contained 10.5% free fatty acids compared to 4.7% for those received at the end of March, 1945. It may be observed, however, that the seeds from Arkansas and Tennessee consistently exhibited less field damage than those from Mississippi and Louisiana.

This observation is confirmed by the yearly averages of free fatty acids, moisture, and oil content in seeds analyzed by the Barrow-Agee Laboratories as shown in Table 55. In 5 out of the 6 seasons covered by this table, the seeds from Arkansas and Tennessee had a lower average free fatty acid content than the seeds from Mississippi and Louisiana.

TABLE 55

Yearly Averages by States of Percentages of Free Fatty Acids, Moisture, and Oil in Cottonseed Received at Oil Mills, 1937–38 to 1943–44[a]

State	F[b]	M[c]	O[d]	F	M	O	F	M	O
	1937–38			1938–39			1940–41		
Mississippi	4.4	12.6	19.0	0.8	10.2	19.5	0.9	13.3	19.0
Arkansas	2.3	12.7	19.3	0.6	9.7	19.1	1.0	13.8	18.2
Louisiana	3.9	11.8	19.0	1.2	11.0	18.4	1.2	13.4	19.2
Tennessee	1.4	13.9	18.9	0.6	10.1	18.7	0.7	13.0	18.3
	1941–42			1942–43			1943–44		
Mississippi	1.3	15.2	19.3	0.6	9.0	19.0	1.1	13.9	18.7
Arkansas	0.8	15.9	18.5	0.9	8.9	19.0	0.7	13.0	18.6
Louisiana	1.9	14.7	18.7	0.8	10.0	18.7	2 6	13.9	18.1
Tennessee	0.6	14.7	18.7	0.5	11.8	18.2	0.7	14.2	17.9

[a] *Barrow-Agee Reports*, Barrow-Agee Laboratories, Memphis, Tennessee.
[b] F = per cent free fatty acids.
[c] M = per cent moisture (wet basis).
[d] O = per cent oil.

A complete lack of correlation between oil and moisture contents of cottonseed and the extent of field damage was reported by Meloy,[73] who based his conclusions upon the results of the examination of thousands of seed grade certificates. It must be remembered, however, that the moisture content of seeds received in mills does not necessarily reflect the moisture content of the seed while in the field. Therefore, Meloy's conclusion that no correlation exists must be considered as tentative until confirmed by experiments conducted in such a manner that the complete history of the seeds is known—from maturation through harvesting and ginning to their ultimate arrival at the mill.

A possible cause of field damage may be deduced from a set of remark-

[73] G. S. Meloy, *Oil & Soap*, **16**, 174–178 (1939).

able observations made by Meloy,[74] who examined the results of analyses of seeds received during the 1943 season from 3 adjacent counties in Mississippi, namely, Leflore, Holmes, and Sunflower Counties. During August, September, and the early part of October, practically all of the seeds received from these counties were of prime or superior quality. Shortly after the first week in October, marked differences began to appear between the seeds received from Sunflower County and those received from the other two counties, as is evident by reference to Table 56.

TABLE 56

Average Free Fatty Acids and Moisture in Cottonseed Produced in Sunflower and Leflore Counties, Mississippi, during the 1943 Season[a]

Constituent	August	September	October	November
Sunflower County				
Average free fatty acids, %	0.48	0.44	0.74	0.99
Average moisture (wet basis), %	8.86	8.98	9.81	10.20
Leflore County				
Average free fatty acids, %	0.62	0.71	3.09	4.42
Average moisture (wet basis), %	8.77	9.57	10.23	10.67

[a] G. S. Meloy, Address, Annual Meeting, National Cottonseed Products Association, New Orleans, May 12–16, 1944.

Although the seeds from Leflore County had a slightly higher moisture content when received at the oil mills than did the seeds from the other two counties, the difference in moisture could scarcely account for the marked differences in the free fatty acid content of the oil.

Subsequent investigation developed the fact that all the cottonseed produced in the immediate vicinity of the Tallahatchie and Yazoo rivers in Leflore and Holmes Counties, as well as that produced in the immediate vicinity of the Big Black river in Holmes County, had a high content of free fatty acids, whereas seeds produced only 20 miles from these rivers invariably had a low content of free fatty acid.

The only significant climatic factor which would tend to influence field damage was observed to be the humidity under which the seeds matured and dried in the boll. Meloy postulated that the areas near the rivers were in a "humidity pocket," whereas Sunflower county was in an area of relatively low atmospheric humidity. Unfortunately, no climatological data appears to have been recorded for these counties that year so that this hypothesis can not be substantiated.

[74] G. S. Meloy, Address, Annual Meeting, National Cottonseed Products Association, New Orleans, May 12–16, 1944.

Meloy visited the 3 afore-mentioned counties and found that the fields located near the rivers were surrounded by swamps and ponds, which resulted in the existence of a relatively high water table during the dry summer months, a condition presumably conducive to heavy growth of foliage on the plants.[75] During the subsequent rainy season which occurred during harvest, the heavy foliage on the cotton plant tended to maintain a high humidity around the bolls. Meloy concluded from his observations that the atmospheric humidity under which cottonseed matures is of prime importance in determining the extent to which field damage may occur. Seeds which had matured under conditions of low humidity suffered little field damage even though they were subsequently exposed to wet weather. Conversely, seeds which matured under very humid conditions became damaged even though the moisture content was subsequently reduced by drying.

When Meloy's observations are considered in the light of the conclusions which may be drawn from the reports of the Barrow-Agee Laboratories, the importance of the location of the growing plant as a contributory factor to field damage becomes more evident. It is obvious that the foregoing conclusions must be tentative, since they involve considerable speculation concerning the conditions actually existing during the growing season. They serve, however, to emphasize the need for undertaking controlled experiments to determine the extent to which field damage is influenced by such environmental conditions as atmospheric humidity.

C. Storage Damage

Storage damage occurs not only in a different locale from field damage, but involves additional environmental factors, especially higher temperatures. Although viable seeds within the cotton boll can produce heat, conditions in bolls are more conducive to dissipation of this heat than in large seed piles. In the field, temperatures remain close to that of the atmosphere, while in storage temperatures may become markedly higher. This difference in the environmental temperature accounts for the previously mentioned difference in the colors observed in cross sections of field-damaged and storage-damaged seeds, and in the inferior quality of products obtained from storage-damaged seeds as compared to field-damaged seeds.

It may be assumed in general that, if a given lot of seed exhibits a marked tendency to heat when stored in bulk, it will deteriorate to some extent even if the temperature is controlled by air or mechanical cooling procedures. Kyame and Altschul [55] found that seeds which were more vigorous than others with respect to respiration—*i.e.*, which had a greater average respiration intensity at equivalent moisture contents—also ex-

[75] G. S. Meloy, *private communication* (1944).

hibited a greater relative vigor with respect to lipolysis. It might be expected that the same relationship would hold with respect to heating and lipolysis.

It has been tacitly assumed in the preceding discussions that enzymatic activity within the seeds is responsible for the biological activity leading to deterioration. In contrast to this view a considerable portion of the literature dealing with seed deterioration during storage is concerned with the contributions of microörganisms to the phenomenon.[76] For example, Ramstad and Geddes [39] have suggested that most of the heating in moist soybeans is due to the action of microörganisms. Milner and Geddes [77] have extended this hypothesis to include the contention that lipolysis in moist soybeans is the result of microbial activity. Other investigators have attributed deterioration in moist flaxseed [40, 50] and wheat [78] to similar causes. Bailey and Gurjar [79] reviewed the status of this question with respect to wheat and Tervet [80] has suggested that molds are the cause of loss of viability in frost-damaged seeds. On the other hand, Pratt,[81] and Allen and Goddard [82] have presented evidence that the increased respiration of mildewed wheat is due to the higher respiration of the host.

Although none of the afore-mentioned researches bear directly on the problem of cottonseed deterioration, they suggest the possibility that microörganisms may constitute a factor which cannot be ignored in considering storage damage of cottonseed. Up to the present time, the elucidation of the relative effects of microörganisms and seed enzymes has proven difficult and no clear-cut experiments have been performed. For example, evidence supplied by Malowan,[38] that surface sterilization of cottonseed does not affect its respiration, does not necessarily imply that microorganisms play no role in respiration. Microörganisms, if present within the seed coat, would be unaffected by this treatment. On the basis of the observation that heat-sterilized soybeans which were subsequently infected with molds respired in a manner similar to ordinary soybeans. Ramstad and Geddes [39] contended that microörganisms are primarily responsible for the respiration observed in the soybean. Such a conclusion may not necessarily be justified since it assumes a passive relationship between parasite and host, whereas the activities of one organism may be and probably are modified by the presence of the other. The behavior of viable and dead seeds do not afford valid comparisons of biological activity.

[76] C. M. Jaeger, *Chemical Changes in Stored Grains,* U.S. Dept. Agr., ACE-191. NM-227, Peoria, Illinois, 1943.
[77] M. Milner and W. F. Geddes, *Cereal Chem.,* **22,** 484–500 (1945).
[78] W. Leach, *Can. J. Research,* **C22,** 150–161 (1944).
[79] C. H. Bailey and A. M. Gurjar, *J. Agr. Research,* **12,** 685–713 (1918).
[80] I. W. Tervet, *Phytopathology,* **35,** 3–15 (1945).
[81] R. Pratt, *Science,* **88,** 62–63 (1938).
[82] P. J. Allen and D. R. Goddard, *Science,* **88,** 192–193 (1938).

Altschul and co-workers [67] have offered another approach to this problem, wherein the effect of a fixed concentration of inhibitor upon a variety of biological activities is measured. If microörganisms are the sole cause of respiration and lipolysis in seeds, the inhibition of the growth of these organisms should effect both of these processes in a similar manner. If, however, most of the deteriorative changes are due to biological reactions within the seeds themselves, it is conceivable that certain activities should be more susceptible to inhibition than others. These investigators found that treatment of seeds with inhibitors (*e.g.*, Nacconal NR), which would inhibit lipolysis, did not necessarily inhibit respiration. In the case of immature cottonseed, they found that they could stimulate lipolysis and simultaneously inhibit respiration. On the basis of these experiments they concluded that the principal deteriorative processes occurring in stored cottonseed are due to the activity of the enzyme systems within the seed.

Olcott and Fontaine [53] were unable to detect the enzyme lipase in a sample of moist cottonseed which was developing free fatty acids at a rapid rate, which could be interpreted as evidence that lipolysis is not due to the activity of a seed enzyme but to other chemical or biochemical causes. However, as previously pointed out, the inability to detect enzyme activity in *in vitro* experiments does not constitute evidence that the enzyme is not present and active within the seed itself.

Arndt [83] investigated the relationship between the internal infection of cottonseed and loss of viability in storage. Instead of using a simple test for germination he used as a criterion of viability the ability of the seed to develop a seedling with a normal primary root, hypocotyl, and cotyledons. Any seeds which developed only two of the above three plant parts were considered abnormal. When he compared the frequency of total nonviability and abnormal viability with internal microbial infection, he found it necessary to conclude that initial loss of viability is probably associated with enzymatic action in the seeds.

It would appear that the question of the relative roles played by seed enzymes and microörganisms in effecting biological changes in seeds during storage requires further investigation and elucidation.

The accumulated results of investigations of the author and his co-workers up to the present indicate that the primary cause of deterioration in stored cottonseed, having a moisture content below 14 to 15%, is the activity of enzymes within the seed. In cottonseed containing more than 15% moisture the initial deterioration appears to be also caused by these enzymes, but as deterioration progresses and the seeds become less viable they probably become increasingly susceptible to infection by

[83] C. H. Arndt, *Phytopathology,* **36,** 30–37 (1946).

microörganisms, and ultimately the activity of the latter may become the predominant factor in the deteriorative process.

XI. Biochemistry of Cottonseed Deterioration

Throughout the preceding discussion two facts predominate: (*a*) that biological activity in stored seeds increases with increasing moisture content of the seed; and (*b*) that the intensity of the biological response to increasing moisture content varies with the history of the seeds. Elucidation of these two phenomena is pertinent to an understanding of the deteriorative processes which occur in cottonseed. Although insufficient information is available for the development of a completely satisfactory theory of cottonseed deterioration during storage, a tentative hypothesis concerning the biological phenomena involved is not entirely unwarranted.

In the life cycle of the plant, the dormant cottonseed represents a relatively inactive state intermediate between two active states. Following pollination, the seed is the seat of vigorous synthetic activity. Energy derived from the growing plant is utilized for the production of tissue and for the synthesis of food reserves. As long as the seed is connected to the remainder of the plant and can derive energy therefrom, synthesis will constitute its primary activity. Biological activity in living organisms generally involves the maintenance of a balance between synthesis and degradation of large molecules. Synthesis predominates when energy is supplied to the organism and an "energy pressure" is produced. As the cottonseed matures, its attachment to the plant weakens and less and less energy is available for synthesis. In a completely mature cottonseed, synthetic activity has ceased or is proceeding at an immeasurably small rate.

If such a state of maturity should be reached under conditions which still favor vigorous enzymatic activity but with the "energy pressure" removed, degradation would be favored. The food reserves which had been previously synthesized would be attacked, and hydrolysis of the fats, carbohydrates, and proteins would ensue. These processes would result in loss of viability and general deterioration. However, maturation is generally accompanied by the creation of conditions which inhibit biological activity. In many seeds this is accomplished by dehydration. Thus, cottonseed which may have a moisture content of 70% or more during the initial stages of development will contain less than 10% when fully matured. Dehydration favors reduction of all enzymatic activity both by reduction of the mobility of the enzymes and substrates within the cells, and by the promotion of adsorption of enzymes on, and integration of the enzymes with, the insoluble cellular constituents—thereby rendering them temporarily inactive.

If a mature seed is exposed to the high-moisture condition required for germination, enzymatic activity is resumed. This renewal of activity does not occur immediately after water is introduced into the system. Only those enzymes which are not firmly bound to the cellular material can react with the substrates which are now made available to them through conditions conducive to increased mobility. Most of the enzymes have to be liberated from the tissues and such a process requires enzymatic hydrolysis. A new "energy pressure" is developed and a new synthetic cycle is initiated. The energy in this case is supplied by the combustion of the food reserves which had been synthesized during the growth of the seed. Under normal conditions such an "energy pressure" is maintained until the young plant is capable of utilizing solar energy for further growth.

The conditions of dehydration during the last stages of maturation are critical in determining the future behavior of the fully matured cottonseed. Freshly opened cotton bolls have a moisture content of about 50%,[22] which may decrease to about 10% in ten days under ideal weather conditions. If, however, rainfall and high atmospheric humidity prevail during the ten-day period following opening of the bolls, field damage will result. Also, if the rate of loss of moisture is greatly reduced or if there are recurring rains so that the moisture content of the seeds alternately increases and decreases during that period, field damage will result.

There is, however, a condition intermediate between ideal drying conditions and those favorable for the occurrence of pronounced (visible) field damage. The seeds may be dried rapidly enough to prevent readily detectable field damage (*e.g.*, loss in viability and formation of free fatty acids) but not rapidly enough or consistently enough to permit orderly integration of the enzymes with the tissue material. A properly dried cottonseed may be compared with a well ordered, neatly stacked pile of bricks and an improperly dried seed, with a pile of bricks heaped together at random. Even though there is no readily detectable field damage, improperly dried seeds may be more sensitive to moisture and, if they become wet in the field or prior to storage, they will tend to deteriorate more readily during storage than normal, well ordered seeds. In properly dried seeds, the enzymes will have been rendered dormant and will resist activation even if the moisture content is later raised, whereas in the other type of seeds the enzymes are more readily susceptible to activation. In the words of Meloy,[73] ". . . the *sine qua non* of low free fatty acid in the oil in cottonseed is an initial dehydration of the plant juices in the seeds within a period of possibly 15 days after maturation of the bolls. That prolongation of conditions that keep the plant juices in their original and natural composition fosters generation of free fatty acids."

On the basis of the foregoing suppositions the conditions which determine the intensity of the biological activity in cottonseed during storage can be redefined in terms of (*a*) their moisture content and (*b*) the nature of dehydration or extent of prior field damage, *visible* or *invisible*. It is understandable, therefore, why at any given moisture content some cottonseed will not readily deteriorate while other cottonseed will require careful handling to retard the tendency toward accelerated biological activity. An explanation is also provided for the fact that field-damaged cottonseed are more difficult to store without heating than prime cottonseed.

XII. Prevention of Deterioration

A. Field Damage

Inasmuch as field damage is primarily a result of unfavorable atmospheric conditions during the period of boll opening, it cannot be readily controlled but it may be possible to minimize the ultimate damage which may otherwise occur.

1. Harvesting Practice

Meloy [73] suggests that, during a rainy and highly humid harvesting season, cotton should not be left in the field in the hope that atmospheric conditions will become more favorable at a later date. It would be wiser to pick the cotton, even in a wet condition, as soon as the bolls have opened and then dry the seed cotton before ginning. The ginned seeds should again be dried before being put into storage, because the drying of the seed cotton has little effect upon the moisture content of the seed.[30]

2. Chemical Defoliation

Conditions favorable for boll drying may be created by chemical defoliation of the cotton plant prior to harvesting.[84] Often the foliage acts as a blanket to retain moisture within the boll. The removal of the foliage permits access of sunlight to the bolls and thereby promotes rapid drying and permits harvesting of practically all of the bolls at one time. The process of dehydration is aided by this means and the extent of field damage is reduced.

3. Hormone Sprays

It was suggested on page 203 that the tendency for field damage to occur appears to be related to the environment (locality) of the growing plant. Farmers and millers in those areas where field damage is prevalent may find it advantageous to investigate the feasibility of employing plant

[84] P. W. Gull, *Mississippi Farm Research*, **6**, No. 8, 7 (1943).

hormone treatment to accelerate maturation so that the bolls can be made to open sooner and thus, possibly, dry under more favorable atmospheric conditions.

B. Storage Damage

1. Evaluation of Seeds

One of the difficulties involved in the storage of cottonseed, as well as other seeds, is the inability of the mill operator to predict accurately the future behavior of the seeds on the basis of the usual analyses which are made at the time the seeds are received at the mill. The moisture content alone does not provide sufficient information for prediction of storage behavior. Robertson and Campbell [54] have stated that cottonseed containing less than 10% moisture (wet basis) can be safely stored; that those over 14% in moisture content will deteriorate; but that cottonseed in the range of 10–14% moisture content may or may not deteriorate, depending on other factors.

Attempts of Larmour *et al.*[40, 50] to define the safe moisture limits for storage of flaxseed, sunflower seed, and wheat as 10.5, 9.5, and 14.5%, respectively, have applicability only to the particular samples of seeds which they examined. What is actually needed is a rapid method of analysis of seeds which will enable the mill operator to estimate the extent of both *visible* and *invisible* biological damage. It is necessary for him to be able to determine the state of dormancy of the enzymes in the seeds. Possible approaches to this problem have been suggested by Kyame [57] and Altschul,[68] who observed that the autolytic activity of cottonseed (rate of internal proteolysis) was greater in seeds which were deteriorating rapidly than in those which were not. Another approach is suggested by the observation of Kyame and Altschul [55] that seeds which exhibit a greater vigor with respect to respiration also possess a greater vigor with respect to lipolysis. It may yet be possible on such a basis to develop a rapid heating or respiration test to be conducted under standard conditions of artificial moistening, which may enable the mill operator to predict pertinent biological properties of seeds which are intended for storage. Any procedure that will make possible a more selective storage procedure will serve to reduce subsequent storage damage.

2. Handling and Storage

There is no doubt that the possibility exists for improvement in present storage procedures. Suitable storage conditions for the maintenance of high viability in seed destined for planting have already been discussed on page 168.

3. Chemical Treatment

Although the feasibility of treating seed with chemicals prior to storage has received some attention, work along these lines has not been commensurate with the possible benefits which more intensive investigation may well afford. Deterioration is a result of the activity of enzyme systems and regardless of its origin, *i.e.*, whether in the seeds or in the associated microörganisms, it is subject to inhibition by numerous chemicals. Chemical treatment of cottonseed prior to or during storage must, in order to be successful, fulfill the following requirements:

(*a*) It must completely inhibit deteriorative action in seeds stored in bulk for a period long enough to allow the mill operator to process them at his convenience without suffering economic loss due to storage damage.

(*b*) It must involve the use of small concentrations of chemicals of such type that there will be no after-effect of treatment on the utilizability of the seed products.

(*c*) It must be readily adaptable to existing methods of handling and storing cottonseed, in order that mill operators may apply it without major modification of existing plant facilities.

(*d*) It must be cheap enough to be economical in those areas where it is most urgently needed.

If the chemical treatment is to be applicable to the storage of seeds for planting, a further specification must be added, namely:

(*e*) It must affect for only a temporary period the enzyme systems in the seeds, so that when they are planted the full viability of the seeds will be restored.

CHAPTER VI

PIGMENTS OF COTTONSEED *

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I. Economic Importance of the Pigments

The economic importance of the pigments of cottonseed is evident from the fact that both the oil and the meal are graded on the basis of color, and sellers may be penalized for off color in these products.[1, 2] Nevertheless, the attention of cottonseed processors has usually been focused on methods designed to give the highest possible yield of oil, with but secondary regard for its color. The official refining tests for crude cottonseed oils are based almost entirely on their method of production and content of free fatty acid. The crude oils are graded and sold to the refiner on the basis of free fatty acid content and refining loss of the crude oil, and the color of the refined oil.[3] Refined oil is sold on the basis of its color after bleaching.

When prime cottonseed is processed according to the usual practice, the oil can generally be reduced to an acceptable color level without undue loss by subsequent refining. However, certain conditions of seed development and storage are known to produce in the seed oil deep colors which are not readily removed by the usual refining procedures. Seed which has been damaged in the field, either by defoliation, drought, high moisture, or premature frosts during development of the bolls, yield deeply colored oils on processing.[4] The crude oil obtained from bolls prematurely opened by frost, or "bollie" seed, rapidly darkens on storage, and mixing "bollie" oil with prime oil is reported to cause rapid deterioration in the color of the latter.[5] Seed stored at a high moisture content or at a high temperature

* Invaluable help in the preparation of this chapter was rendered by K. S. Markley, C. M. Hall, L. E. Castillon, R. T. O'Connor, C. H. Billett, and Leah Katz.

[1] National Cottonseed Products Association, *Rules Governing Transactions between Members,* 1947–1948.

[2] See also pp. 530–534.

[3] American Oil Chemists' Society, *Official and Tentative Methods,* 2nd ed., Chicago, 1947.

[4] G. S. Meloy, *Cotton and Cotton Oil Press,* **44,** No. 23, 14–16 (1943).

[5] R. H. Fash, *Oil & Soap,* **11,** 106 (1934).

develop dark colors in the oil.[6] However, in spite of the frequent occurrence of objectionable colors in cottonseed oils, special refining procedures are not available for their removal. The processor's only recourse in the refining of oils containing unusually high quantities of pigments is the use of stronger lye, more bleaching clay, or re-refining. Any of these will reduce the yield of the finished product. It can be concluded that the lack of knowledge of methods for controlling the effect of cottonseed pigments results in serious losses to the cottonseed grower and processor.

From the point of view of the scientist, the pigments of cottonseed present a thoroughly interesting and, as yet, unsolved problem. Extensive investigations of the chemistry of gossypol, the principal pigment of the kernel, have shown it to be a complex polyphenolic,[7, 8] dicarbonyl [9] compound, which exhibits such a variety of reactions that efforts to identify it with any known class of organic compounds [10, 11] have been fruitless. Most of the pigments of the kernel are concentrated in distinct morphological structures, known as pigment glands, which are scattered throughout the tissue of all the parts of the kernel except the radicle. Pigment glands of this type have been reported to be peculiar to cottonseed and the seed of a very few closely related genera.[12, 13] Very little is known of the behavior or the function of either the pigments or the glands in the seed.

Until recently, in spite of the dark color of the pigment glands in the seed, and the red to blue-black color of oils derived from cooked seed, the attention of both chemists and technologists has been devoted almost exclusively to gossypol, a pale yellow pigment.[14] Investigations of the chemical properties of gossypol have shown it to undergo alteration to more deeply colored compounds under a variety of conditions. It has also been shown that gossypol largely disappears as such during the processing of cottonseed, but there has been little other than conjecture concerning its ultimate fate in cottonseed products. Attempts to correlate the chemistry of the pigments of cottonseed with processing have been few.

Efforts of technologists have been primarily concentrated on the elimination of gossypol and other pigments of cottonseed rather than with the utilization or conversion of these pigments to forms which might increase the value of the derived products. The "nuisance value" of gossypol is so great that it has even been suggested that plant breeders

[6] J. Malowan, *Oil & Fat Ind.*, **4,** 127–130 (1927).
[7] L. Marchlewski, *J. prakt. Chem.*, **60,** 84–90 (1899).
[8] F. E. Carruth, *J. Am. Chem. Soc.*, **40,** 647–663 (1918).
[9] E. P. Clark, *J. Biol. Chem.*, **75,** 725–739 (1927).
[10] P. Karrer and E. Tobler, *Helv. Chim. Acta,* **15,** 1204–1212 (1932).
[11] R. Adams and Z. W. Wicks, *J. Am. Chem. Soc.*, **66,** 1315–1316 (1944).
[12] E. E. Stanford and A. Viehoever, *J. Agr. Research,* **13,** 419–437 (1918).
[13] R. G. Reeves, *Am. J. Botany,* **23,** 394–405 (1936).
[14] F. Mayer, *The Chemistry of Natural Coloring Matters,* translated and revised by A. H. Cook, Reinhold, New York, 1943, pp. 114–117.

should attempt to develop gossypol-free strains of cottonseed.[15] However, it has been estimated that, if some industrial use could be found for gossypol, it could be obtained in amounts as high as 40,000 tons annually.[16] Gossypol possesses pronounced antioxidant properties [17] and should have applications in this capacity. The polyphenolic nature of gossypol suggests a variety of additional uses either directly or as an intermediate in the production of antiseptics, pharmaceuticals, plastics, or explosives.

In the following pages, an attempt is made to present an adequate review of the significant contributions which have been made to the chemistry of gossypol and other pigments of cottonseed, of their occurrence and behavior in the seed, and of their interconversions during processing of the seed. A brief summary of present knowledge of the pigments of cottonseed hulls has also been included. It is hoped that assembling these data will serve to indicate more fruitful approaches to solution of the problems of their structure, function in the seed, control during processing of the seed, and ultimate utilization.

II. Chemistry of the Pigments of Cottonseed

A. Gossypol

1. Isolation and Purification

The first isolation of a yellow pigment from cottonseed was recorded by an English chemist [18] in 1886. The crude yellow compound, which was reported to act as a fast dye for silk and wool, was isolated from the foots obtained in alkali refining of expressed cottonseed oil. Several years later, a Polish chemist, Marchlewski,[7] purified the pigment obtained from the same source. For this purpose he employed the ether-insoluble product obtained by reaction of the pigment with acetic acid. He demonstrated the polyphenolic character of the compound and named it gossypol, from gossyp(ium phen)ol, to indicate both its origin in cottonseed and its chemical nature.

Carruth,[8] investigating gossypol many years later in connection with "cottonseed injury," developed improved procedures for the isolation of gossypol from crude ethereal extracts of cottonseed. His methods were based on the properties of three derivatives: the ether-insoluble compounds formed, respectively, by the reaction of gossypol with acetic acid and with aniline, and the water-soluble sodium salt of gossypol. The three

[15] M. I. Smirnova, *Bull. Applied Botany Genetics Plant Breeding U.S.S.R.* **Ser. III,** No. 15, 227–240 (1936) (English summary, p. 240); *Chem. Abst.*, **31,** 5482 (1937).
[16] H. S. Olcott, *Cotton and Cotton Oil Press,* **43,** No. 7, 22–25 (1942).
[17] H. A. Mattill, *J. Biol. Chem.*, **90,** 141–151 (1931).
[18] J. Longmore, *J. Soc. Chem. Ind.*, **5,** 200–205 (1886).

basic methods developed by Carruth and employed by most subsequent investigators of gossypol may be briefly described as follows:

Method 1: A concentrated ethereal extract of cottonseed is treated with 80% aqueous acetic acid in amounts equal to one-half to one-third of the volume of the extract. Upon warming the mixture, and then allowing it to stand for some time, gossypol-acetic acid precipitates, leaving most of the other extract components in solution. Preliminary defatting of the seed by extraction with hydrocarbon solvents accelerates the subsequent precipitation of gossypol-acetic acid. Adhering oil is removed by washing the precipitate with light petroleum naphtha. To remove bound acetic acid, the crude gossypol-acetic acid is hydrolyzed by dissolving it in ether and heating the ethereal solution in contact with water containing a small amount of sodium dithionite, until all of the ether has evaporated. For further purification, gossypol is reprecipitated as gossypol-acetic acid, and the process is repeated until no further purification can be obtained by this means. The gossypol-acetic acid is hydrolyzed as described above, and recrystallized from organic solvents.

Method 2: A crude ethereal extract of cottonseed is shaken with a slight excess of dilute aqueous sodium hydroxide. This results in the extraction of the sodium salts of gossypol and the fatty acids into the aqueous layer. Addition of a reducing agent, preferably sodium dithionite, to the alkaline solution prevents oxidative decomposition of the gossypol. The gossypol obtained by acidification of the alkaline extract is purified through its compound with acetic acid.

Method 3: Aniline, in the amount of about 5% of the weight of the extract, is added to an ethereal extract of cottonseed; the mixture is heated for a short time on a water bath and then set aside until precipitation is practically complete. This may require a week or more, but preliminary defatting of the seed increases the rate of precipitation. The resulting precipitate is washed with ether and recrystallized from aniline. It is then dissolved in hot alcoholic potassium hydroxide and the aniline is removed by steam distillation. A small portion of sodium dithionite is added to the resultant solution to suppress the formation of oxidation products, after which it is acidified to precipitate gossypol. The gossypol is then purified as gossypol-acetic acid.

Subsequent procedures published for the isolation of gossypol have introduced only slight modifications of Carruth's methods. The procedure most commonly employed has been the first method of Carruth, *i.e.*, ether extraction of defatted cottonseed followed by precipitation and subsequent purification of gossypol-acetic acid.[9, 19-30] It has recently been

[19] E. W. Schwartze and C. L. Alsberg, *J. Agr. Research,* **28,** 191–198 (1924).
[20] E. P. Clark, *Oil & Fat Ind.,* **6,** 15–19 (1929).
[21] J. O. Halverson and F. H. Smith, *Ind. Eng. Chem., Anal. Ed.,* **5,** 29–33 (1933).
[22] L. Schmid and S. Margulies, *Monatsh.,* **65,** 391–398 (1935).
[23] M. Podol'skaia, *Fettchem. Umschau,* **42,** 96–100 (1935).
[24] L. K. Kozhevnikova and V. E. Gil'tburg, *Masloboino Zhirovoe Delo,* **12,** 545–546 (1936); *Chem. Abst.,* **31,** 5194 (1937).

reported that preliminary defatting is unnecessary if the extraction is carried out at room temperatures.[31]

Isolation of gossypol by alkaline extraction of ethereal cottonseed extracts (Method 2) has proved useful [32–34] for the preparation of relatively large quantities of gossypol from ethereal extracts of cottonseed, when preliminary defatting is inexpedient and prolonged contact of the extracted material with the solvent at elevated temperatures cannot be avoided conveniently.

A modification of Carruth's third method, namely, isolation of gossypol with the use of aniline, was recently employed [35] for the separation of gossypol from chloroform extracts of nondefatted cottonseed. The use of alcoholic sodium hydroxide as recommended by Carruth, or of concentrated sulfuric acid [36] was reported to be unsatisfactory for the decomposition of any but very small quantities of dianilinogossypol. However, excellent yields of gossypol-acetic acid were obtained from 5-g. samples of crude dianilinogossypol when they were dissolved in warm acetic anhydride and the solution poured into water as rapidly as possible. During the afore-mentioned investigation it was observed that solid gossypol-acetic acid is conveniently hydrolyzed by heating it in contact with boiling water.

A method [37] recently devised for the rapid extraction of gossypol from cottonseed kernels for analytical purposes is readily adapted to the rapid isolation of large quantities of gossypol. Finely ground or flaked seed is thoroughly mixed with 30% aq. ethanol; the suspension is allowed to stand with occasional agitation for a minimum of ten minutes. Sufficient ethanol is then added with stirring to yield an extract containing 60% ethanol, after which the extract is freed of residual meal by centrifuging or filtering. Ether is added to the aqueous ethanolic extract, and then water in quantities sufficient to cause the gossypol to precipitate from the aqueous

[25] K. N. Campbell, R. C. Morris, and R. Adams, *J. Am. Chem. Soc.*, **59,** 1723–1728 (1937).

[26] F. H. Smith and J. O. Halverson, *Ind. Eng. Chem., Anal. Ed.*, **11,** 475 (1939).

[27] H. D. Royce, J. R. Harrison, and P. D. Deans, *Ind. Eng. Chem., Anal. Ed.*, **12,** 741–744 (1940).

[28] C. M. Lyman, B. R. Holland, and F. Hale, *Ind. Eng. Chem., Anal. Ed.*, **15,** 489–491 (1943).

[29] C. H. Boatner, *Oil & Soap,* **21,** 10–15 (1944).

[30] E. L. Hove and Z. Hove, *J. Biol. Chem.*, **156,** 623–632 (1944).

[31] F. H. Smith and J. O. Halverson, *Oil & Soap,* **23,** 361–363 (1946).

[32] C. H. Boatner, M. Caravella, and C. S. Samuels, *J. Am. Chem. Soc.*, **66,** 838 (1944).

[33] C. H. Boatner, C. S. Samuels, C. M. Hall, and M. C. Curet, *J. Am. Chem. Soc.*, **69,** 668–672 (1947).

[34] C. H. Boatner, R. T. O'Connor, C. S. Samuels, and M. C. Curet, *J. Am. Chem. Soc.*, **69,** 1268–1271 (1947).

[35] V. K. Murty, K. S. Murty, and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **A16,** 54–61 (1942).

[36] E. P. Clark, *J. Biol. Chem.*, **76,** 229–235 (1928).

[37] F. H. Smith, *Ind. Eng. Chem., Anal. Ed.*, **18,** 43–45 (1946).

layer and dissolve in the ether layer. Gossypol-acetic acid is obtained by the addition of acetic acid to the ether extract.

Since the isolation of gossypol is laborious and time-consuming, regardless of procedure, the choice of methods should be determined by the availability of the raw material. If the primary objective of the investigation is the preparation of pure gossypol, and adequate facilities are available and time is not an important consideration, Method 1 of Carruth provides the least laborious procedure. On the other hand, if crude extracts of nondefatted cottonseed are readily available, Method 2 of Carruth is the most useful since it can be applied to extracts obtained with the use of any water-immiscible solvent. If speed of preparation is most desired, extraction of gossypol from cottonseed with the use of mixtures of water and water-miscible organic solvents, followed by transfer to ether, provides the most advantageous procedure.

Although the foots from refining of crude hydraulic-pressed oils constituted the first source of gossypol,[7, 18] expressed cottonseed oils produced by modern processing methods contain little, if any, unchanged gossypol. Consequently, even if there were no additional disadvantages, foots from expressed oils no longer provide a satisfactory source of gossypol. On the other hand, the foots obtained from alkali-refining of solvent-extracted cottonseed oil contain large quantities of gossypol, provided the oil is extracted with a solvent which also extracts the gland pigments.[38, 39] The foots should be suspended in water containing a small amount of sodium dithionite and the gossypol separated according to the recently published modification [34] of Carruth's second method.

Royce, Harrison, and Hahn [40] recommend the use of cotton-root bark as a source of gossypol because of its relatively high gossypol content and freedom from oil.

If available, separated pigment glands prepared by the flotation process for the mechanical fractionation of cottonseed [41] serve as an ideal source for the isolation of gossypol. Gossypol constitutes 30 to 50% of the weight of the pigment glands and is usually accompanied by only very small quantities of other pigmented material. Preliminary rupture of the walls of the glands by moistening or grinding them with sharp sand permits rapid extraction of gossypol [42] by use of any solvent in which this pigment is soluble. Contact with diethyl ether at 38° F. for twenty-four hours yields complete extraction of gossypol with a minimum amount of

[38] C. H. Boatner, R. T. O'Connor, C. M. Hall, L. E. Castillon, and M. C. Curet. *J. Am. Oil Chem. Soc.*, **24**, 276–283 (1947)

[39] C. H. Boatner, R. T. O'Connor, C. M. Hall, and L. E. Castillon, *Botan. Gaz.*, **109**, No. 2 (Dec., 1947).

[40] H. D. Royce, J. R. Harrison, and E. R. Hahn, *Oil & Soap*, **18**, 27–29 (1941).

[41] C. H. Boatner and C. M. Hall, *Oil & Soap*, **23**, 123–128 (1946).

[42] C. H. Boatner, C. M. Hall, M. L. Rollins, and L. E. Castillon, *Botan. Gaz.*, **108**, 484–494 (1947).

decomposition. Glacial acetic acid is added to the ethereal extract and the mixture is warmed until gossypol-acetic acid begins to precipitate. The gossypol-acetic acid obtained by this means is usually sufficiently pure for many purposes.

2. Physical Properties and Composition

Gossypol is a yellow solid which has been reported to be soluble in cold dioxane, diethylene glycol, methanol, ethanol, isopropanol, *n*-butanol, ether, ethyl acetate, acetone, chloroform, carbon tetrachloride, and pyridine; slightly soluble in glycerol, cyclohexane, and high-boiling petroleum naphtha (b.p. 60–110° C.), and insoluble in low-boiling petroleum naphtha (b.p. 30–60° C.) and water.[25]

When heated, gossypol melts with decomposition. As shown in Table 57, the temperatures at which pure gossypol has been reported by different investigators to decompose do not agree. Clark, who isolated large quantities of gossypol for investigation of its chemical properties, first noted these discrepancies. He concluded that the variation in the decomposition temperatures of gossypol was relatively unimportant, since he found that gossypol preparations having widely different decomposition temperatures (199°, 205°, and 214° C.) were identical with respect to other properties.[36] However, he reported only the crystallographic properties and elementary composition for the three preparations and did not state whether their chemical properties had been compared. It is always difficult to establish the melting point of an organic compound with any degree of accuracy when it is thermally unstable and melts with decomposition at a relatively high temperature. Nevertheless, the difference in the melting points of the lowest melting (180° C.) form of gossypol and the highest melting (214° C.) form appears to be beyond the range which can be attributed to differences in the method of determining the melting point.

Campbell, Morris, and Adams [25] attributed the differences in the melting point of gossypol to polymorphism, since they were able to obtain gossypol which melted at 184°, 199°, and 214° C. by employing different solvents for its recrystallization. However, as pointed out by Murty, Murty, and Seshadri,[35] and as shown in Table 57, this does not appear to provide a satisfactory explanation for all of the differences observed. For example, in the hands of different investigators, recrystallization from ether and petroleum naphtha has yielded gossypol melting at 180°, 184°, 189°, and 199° C. Recrystallization from ether and water has yielded gossypol melting at 184° and at 214° C. (Table 57).

Some of these differences might have been caused by application of heat during recrystallization. Since it has been shown [29] that gossypol is unstable in solution at room temperature, it may be concluded that it would decompose or rearrange rapidly at higher temperatures. Conse-

TABLE 57

Melting Point, Crystalline Form, Elementary Composition, and Molecular Weight of Gossypol

Solvent used for recrystallization	M.p., °C.	Crystalline form	Composition, %[a]		Molecular weight
			Carbon	Hydrogen	
Ethanol–water[b]	186–190	—	67.76	5.48	574,[c] 538[d]
Ethanol–water[e]	199[f]	Plates	69.44	6.01	571[g]
Ethanol–water[h]	—	—	69.75	6.02	—
Ether–methanol[e]	214[f]	Plates	69.49	6.00	572[i]
Ether–ethanol[j]	—	Prisms	69.48	5.83	—
Ether–methanol[k]	205[f]	—	69.49	5.86	—
Ether–water[e]	214[f]	Plates	69.40	5.94	506[d]
Ether–water[l]	181–181.5[f]	Powder	68.45	5.88	—
Ether – petroleum naphtha[m]	199	—	69.69	5.80	—
Ether – petroleum naphtha[n]	184	—	69.67	5.97	—
Ether – petroleum naphtha[o]	184	Needles	—	—	518[d]
Ether – petroleum naphtha[p]	180	Needles	—	—	518[d]
Ether – petroleum naphtha[q]	189[r]	Rectangular plates	69.3	5.9	—
Ether – petroleum naphtha[s]	183.5[f]	Dog-toothed prisms	66.72	6.21	—
Toluene[t]	184[f]	Powder	[u]	[u]	—

[a] Calculated for $C_{30}H_{30}O_8$: mol. wt., 518; C, 69.50; H, 5.79. Calculated for $C_{30}H_{28}O_9$: mol. wt., 532; C, 67.67; H, 5.26. Calculated for $C_{30}H_{30}O_9$: mol. wt., 534; C, 67.40; H, 5.62. Calculated for $C_{30}H_{32}O_9$: mol. wt., 536; C, 67.16; H, 5.97. Calculated for $C_{32}H_{34}O_{11}$: mol. wt., 558; C, 68.81; H, 5.38.

[b] Gossypol isolated as gossypol-acetic acid from ethereal extract of defatted cottonseed, F. E. Carruth, *J. Am. Chem. Soc.*, **40**, 647–663 (1918).

[c] By elevation of boiling point of ether and of acetone. [d] By alkaline titration.

[e] Gossypol isolated as in footnote *b*, E. P. Clark, *J. Biol. Chem.*, **75**, 725–739 (1927).

[f] Temperature corrected for stem exposure. [g] By depression in f. p. of camphor.

[h] Gossypol isolated as in footnote *b*, L. K. Kozhevnikova and V. E. Gil'tburg, *Masloboino Zhirovoe Delo*, **12**, 545–546 (1936); *Chem. Abst.*, **31**, 5194 (1937).

[i] By depression of freezing point of camphor.

[j] Gossypol isolated as in footnote *b*, M. Podol'skaia, *Fettchem. Umschau*, **42**, 96–100 (1935); composition and optical-crystallographic properties, M. Podol'skaia, *Biochem. Z.*, **284**, 401–411 (1936).

[k] Gossypol isolated by decomposition in concentrated sulfuric acid of precipitate from aniline extract of cooked cottonseed, E. P. Clark, *J. Biol. Chem.*, **76**, 229–235 (1928).

[l] Gossypol isolated by alkaline extraction of ethereal extract of cottonseed, C. H. Boatner, M. Caravella, and L. Kyame, *Ind. Eng. Chem., Anal. Ed.*, **16**, 566–572 (1944).

[m] Gossypol isolated as in footnote *b*, P. Karrer and E. Tobler, *Helv. Chim. Acta*, **15**, 1204–1212 (1932).

[n] Gossypol isolated as in footnote *b*, L. Schmid and S. Margulies, *Monatsh.*, **65**, 391–398 (1935).

[o] Gossypol isolated as in footnote *b*, H. D. Royce, J. R. Harrison, and P. D. Deans, *Ind. Eng. Chem., Anal. Ed.*, **12**, 741–744 (1940).

[p] Gossypol isolated as in footnote *b*, from cotton-root bark, H. D. Royce, J. R. Harrison, and E. R. Hahn, *Oil & Soap*, **18**, 27–29 (1941).

[q] Gossypol isolated by decomposition in acetic anhydride of aniline precipitate from chloroform extract of cottonseed, V. K. Murty, K. S. Murty, and T. R. Seshadri *Proc. Indian Acad. Sci.*, **A16**, 54–61 (1942).

[r] Same form was obtained from chloroform and ether.

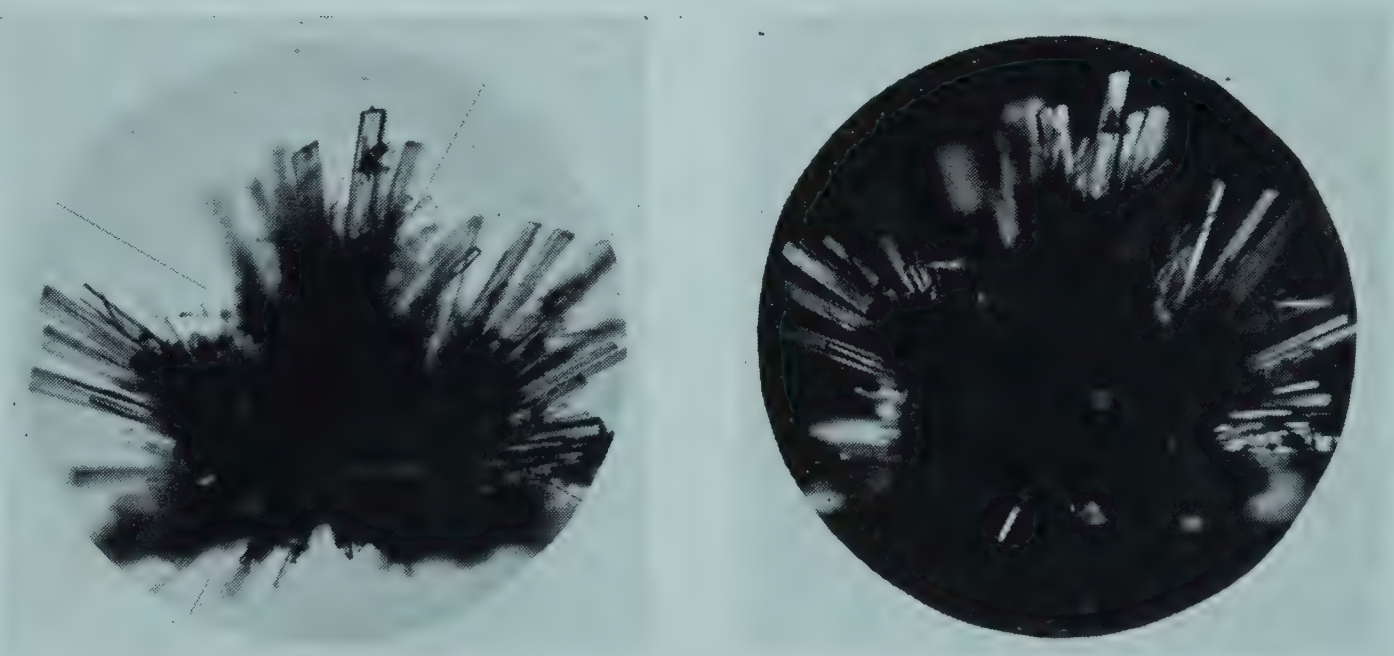
[s] Gossypol isolated as in footnote *l*, C. H. Boatner, R. T. O'Connor, M. C. Curet, and C. S. Samuels, *J. Am. Chem. Soc.*, **69**, 1268–1271 (1947).

[t] Gossypol isolated as in footnote *b*, C. H. Boatner, *Oil & Soap*, **21**, 10–15 (1944).

[u] Analysis after three years: C, 70.49; H, 6.16.

quently, all recrystallizations of gossypol performed by the author have been carried out either at room temperature, if precipitation is rapid, or in a refrigerator at 3.3° C. (38° F.), if precipitation is slow. By observance of these precautions, gossypol melting at 184° C. can be obtained by recrystallization from a mixture of ether and petroleum naphtha, or from toluene. Gossypol obtained by evaporating ethereal solutions of gossypol-acetic acid in contact with hot water has been found to melt at 181–181.5° C., and after one recrystallization from a mixture of ether and petroleum naphtha at 182–183.5° C.

Optical-crystallographic data have been reported for only a few gossypol preparations. Clark [9] reported the properties of crystalline gossypol (m.p. 199° C.), obtained from aqueous ethanol, to be as follows: $\alpha = 1.605$, $\beta = 1.740$, and $\gamma =$ approximately 1.83. Gossypol (m.p. 205° C.) prepared by decomposition of the precipitate obtained by aniline extraction of cooked cottonseed and recrystallized from a mixture of methanol and ether was reported by Clark [36] to exhibit an α-refractive index of 1.605.



(a) (b)

Fig. 41. Photomicrographs (×31) of crystalline gossypol (a) in ordinary light and (b) between crossed Nicols.[34] (By M. E. Jefferson and F. B. Kreeger.)

Podol'skaia reported [43] optical-crystallographic data on gossypol recrystallized from a mixture of ether and ethanol, as follows: crystalline form, prisms or irregular plates; strongly birefringent with regularly oblique extinction; angle of optic axis, two to three times average; optic sign, positive; dispersion of optic axes, g greater than p; refractive indices measured in white light, $n_g = 1.784$, $n_m =$ approximately 1.635.

Crystalline gossypol after purification and three successive recrystallizations from a mixture of ether and petroleum naphtha (Skellysolve F) has been obtained [34] as large clusters of *dog-toothed* prisms (Fig. 41) exhibiting apparent birefringence.

[43] M. Podol'skaia, *Biochem. Z.*, **284**, 401–411 (1936).

On the basis of the elementary composition and the results of alkaline titration of gossypol, as well as the elementary composition and molecular weight of several of its derivatives, Clark [9] proposed the molecular formula, $C_{30}H_{30}O_8$, for gossypol. Several investigators [27, 40, 44] have since reported values for the molecular weight, as obtained by alkaline titration, to be in even better agreement with the formula, $C_{30}H_{30}O_8$, than the values reported by Clark. As shown in Table 57, the elementary analyses of most gossypol preparations for which such data have been reported agree closely with the values calculated for $C_{30}H_{30}O_8$. There seems to be little reason to doubt the correctness of the molecular formulas assigned to gossypol derivatives for which supplementary data such as nitrogen, acetyl, or methoxyl values can be obtained. However, in the absence of such supplementary data, as in the case of gossypol, it is apparent that the carbon, hydrogen, and molecular weight data alone do not provide unequivocal criteria for establishing molecular formulas. For example, the values calculated for the molecular formula $C_{32}H_{34}O_{11}$, which was proposed by Carruth [8] on the basis of Marchlewski's analytical data for lead gossypolate,[7] are very similar to those calculated for $C_{30}H_{30}O_8$.

Adams and Dial reported [45] that consistent elementary analyses of gossypol agreeing with values calculated for $C_{30}H_{30}O_8$ were almost impossible to obtain with their preparations of gossypol. Different samples of gossypol prepared by the author [29, 34, 46] decomposed at temperatures within a range of 3°, and the specific extinction coefficients of their chloroform solutions at 286 and 363–366 mμ, the location of the principal absorption bands of gossypol in chloroform solution,[34] agreed within 10 units. However, their elementary analyses differed and did not agree with the values calculated for $C_{30}H_{30}O_8$. As shown in Table 57, gossypol (m.p. 181–181.5° C.) obtained by hydrolysis of an ethereal solution of gossypol-acetic acid in contact with hot water contained 68.45% carbon and 5.88% hydrogen. Upon recrystallization from a mixture of ether and petroleum naphtha (Skellysolve F), the melting point was raised to 182.5–183.5°, and the carbon and hydrogen contents were found to be 66.72 and 6.21%, respectively. Three independent preparations of gossypol, isolated from cottonseed by different procedures but all finally recrystallized from a mixture of ether and petroleum naphtha (Skellysolve F), exhibited melting points within the range 181° to 185° C., and had carbon and hydrogen contents ranging from 66.72 to 66.82%, and from 6.21 to 6.24%, respectively.

[44] F. H. Smith, *private communication* (1946).
[45] R. Adams and W. R. Dial, *J. Am. Chem. Soc.*, **61**, 2077–2082 (1939).
[46] C. H. Boatner, M. Caravella, and L. Kyame, *Ind. Eng. Chem., Anal. Ed.*, **16**, 566–572 (1944).

Clark pointed out [9] that the use of mixtures of ether and petroleum naphtha for the recrystallization of gossypol yielded a product the elementary analysis of which did not agree with the values calculated for $C_{30}H_{30}O_8$. On the assumption that the latter values were correct, Clark attributed the discrepancies to the retention of solvent of crystallization and employed other solvent mixtures for the purification procedure. However, as previously pointed out, Clark, as well as most subsequent investigators, purified gossypol by recrystallization from hot solvents. Such treatment might well result in some alteration of the heat-sensitive gossypol molecule. In view of these observations, and the absence of any conclusive evidence for the complete structure of gossypol, it would appear that the molecular formula of gossypol has not yet been incontrovertibly established.

3. Chemical Properties

The complexity of the structure of gossypol is manifested in the variety of reactions which the compound undergoes. It reacts as a strong dibasic acid, forming neutral disodium and dipotassium salts which are colored a deeper yellow than the free compound. It is readily soluble in dilute aqueous sodium hydroxide, potassium hydroxide, and sodium carbonate; and dissolves slowly in dilute aqueous sodium bicarbonate, disodium hydrogen phosphate, and in solutions of calcium, barium, and ammonium hydroxides. Solutions of gossypol in ammonium hydroxide yield gelatinous precipitates upon standing. Lead and ferric gossypolate are insoluble in water.

Ethyl alcohol solutions of gossypol and ethyl alcohol and water solutions of its alkali and alkaline earth salts are extremely sensitive to oxidizing agents. They are readily decomposed by Fehling's solution, ammoniacal silver nitrate, ferric chloride, hydrogen peroxide, and a variety of other oxidizing agents, including the oxygen of the air.[7, 8]

Gossypol reacts with organic bases, such as aniline [47, 48] and pyridine,[25, 27] and with liquid ammonia [49] to form nonionic compounds of widely different stabilities. With aliphatic acids, gossypol forms compounds containing one molecule of the acid per molecule of gossypol. These compounds are readily decomposed by exposure to heat or moisture into gossypol and the original aliphatic acid.[8, 25] Gossypol does not react with picric acid.[35]

With the appropriate carbonyl reagent, gossypol forms a stable dioxime,[9] dihydrazone,[10] and di-2,4-dinitrophenylhydrazone. A stable

[47] F. E. Carruth, *J. Biol. Chem.*, **32,** 87–90 (1917).
[48] K. S. Murty and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **A16,** 141–145 (1942).
[49] R. F. Miller and R. Adams, *J. Am. Chem. Soc.*, **59,** 1736–1738 (1937).

compound, gossypol diacetonate, is formed by reaction of gossypol with acetone.[8]

In its capacity as a polyphenol, gossypol readily forms stable esters [9, 50] and ethers.[51–53] Because of the greater stability of these derivatives, their reactions have generally been investigated in preference to those of the free phenol. Gossypol does not react with phenylisocyanate.[35]

Prolonged heating of gossypol at temperatures slightly above its melting point results in the elimination of two molecules of water with the formation of an orange-colored compound, designated *anhydrogossypol.* Anhydrogossypol exhibits properties very similar to those of gossypol.[8, 9, 49]

Upon heating a suspension of sodium gossypolate in strong aqueous sodium hydroxide, two molecules of formic acid are obtained as a by-product and there is formed a colorless polyphenolic degradation product of gossypol, designated *apogossypol.*[54] This strongly acidic polyphenol is very much more unstable than gossypol, but it readily forms stable ethers and esters.[54, 55]

Those derivatives of gossypol which have been investigated most extensively or have served as intermediates for the preparation and investigation of further derivatives are described in some detail in the succeeding sections.

4. Amino Derivatives of Gossypol

The compositions and melting points of the anilino and amino derivatives of gossypol reported by different investigators are shown in Table 58.

The reaction of gossypol with aniline to form a stable insoluble compound was first noted by Carruth.[47] He made this reaction the basis of a method for the determination of gossypol in cottonseed and cottonseed meal. Although Carruth first reported the compound to be dianilinogossypol, he subsequently obtained nitrogen analyses which lead him to suggest the formula [8] to be $2\,C_{30}H_{28}O_9 \cdot 5\,C_6H_5NH_2$. Upon further investigation of the compound which gossypol forms with aniline, Clark [9] reported analyses showing that one molecule of gossypol and two molecules of aniline react with the loss of two molecules of water to form dianilinogossypol. Clark also demonstrated [36] that dianilinogossypol is the compound formed when cooked cottonseed is digested with hot aniline.

Dianilinogossypol is formed rapidly upon solution of gossypol in warm aniline or by addition of aniline to a warm solution of gossypol in ether, chloroform, or benzene. It is insoluble in most of the usual organic sol-

[50] R. F. Miller, D. J. Butterbaugh, and R. Adams, *J. Am. Chem. Soc.*, **59,** 1729–1731 (1937).
[51] R. C. Morris and R. Adams, *J. Am. Chem. Soc.*, **59,** 1731–1735 (1937).
[52] R. Adams and T. A. Geissman, *J. Am. Chem. Soc.*, **60,** 2163–2166 (1938).
[53] K. S. Murty and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **A16,** 146–150 (1942).
[54] E. P. Clark, *J. Biol. Chem.*, **78,** 159–166 (1928).
[55] R. Adams and D. J. Butterbaugh, *J. Am. Chem. Soc.*, **60,** 2174–2180 (1938).

vents, is stable to heat, and is not readily decomposed. Because of its insolubility and stability, its formation has served as the basis of most of the many published methods for the determination of gossypol in cottonseed and cottonseed products. As previously noted, it has also proven useful for the isolation of gossypol from cottonseed extracts. Dianilinogossypol is decomposed upon solution in methanolic potassium hydroxide,[8] concentrated sulfuric acid,[9] or acetic anhydride.[35]

Recently, tetraanilinogossypol was obtained [48] when gossypol was treated with an excess of aniline and heating of the precipitate was avoided. On application of heat, tetraanilinogossypol readily loses 2 molecules of aniline to form dianilinogossypol. In view of the number of times that the reaction of gossypol with aniline has been investigated since its discovery by Carruth in 1917, the delayed isolation of tetraanilinogossypol must be attributed to its instability to heat and the fact that dianilinogossypol has usually been heated to constant weight before analysis. It is significant that in his second report on the anilino derivative of gossypol Carruth [8] found that some of his preparations contained more nitrogen than could be accounted for on the basis of dianilinogossypol.

It is apparent from the data in Table 58 that, as so frequently occurs in gossypol derivatives, two independent groups of investigators obtained

TABLE 58

Amino Derivatives of Gossypol

Name	M.p., °C.	Formula	Elementary composition, %					
			Calculated			Found		
			C	H	N	C	H	N
Dianilinogossypol[a]	302–302	$C_{42}H_{40}N_2O_6$	75.43	6.03	4.19	75.40	6.14	4.13[b]
Tetraanilinogossypol[c]	180[d]	$C_{54}H_{54}N_4O_6$	75.9	6.3	6.6	76.0	6.3	6.8
o-Phenylenediaminogossypol[e]	251–258	$C_{36}H_{34}N_2O_6$	73.1	5.6	4.74	73.24	5.72	4.70
Di-*o*-phenylenediaminogossypol[f]	246[g]	$C_{42}H_{42}N_4O_6$	72.13	6.06	8.02	71.95	5.96	8.08
Di-β-naphthylaminogossypol[f]	310–313	$C_{50}H_{44}N_2O_6$	78.09	5.97	3.65	77.95	5.78	3.69
Diaminogossypol[h]	228–230	$C_{30}H_{32}N_2O_6$	69.76	6.20	5.42	69.56	6.53	5.17

[a] E. P. Clark, *J. Biol. Chem.*, **75**, 725–729 (1927).
[b] Molecular weight (Rast) 680, 650; calculated for dianilinogossypol, 668.5.
[c] K. S. Murty and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **A16**, 141–145 (1942).
[d] Evolves aniline at 180°C., then melts at 303°C.
[e] P. Karrer and E. Tobler, *Helv. Chim. Acta*, **15**, 1204–1212 (1932).
[f] R. Adams, C. C. Price, and W. R. Dial, *J. Am. Chem. Soc.*, **60**, 2158–2160 (1938).
[g] A product melting at 184°C. is sometimes obtained, but the melting point on drying and long standing changes to 246°C.
[h] R. F. Miller and R. Adams, *J. Am. Chem. Soc.*, **59**, 1736–1738 (1937).

entirely different compounds by reaction of gossypol with the same reagent, in this case, *o*-phenylenediamine. Karrer and Tobler [19] obtained *o*-phenylenediaminogossypol, whereas Adams, Price, and Dial [56] obtained di-*o*-phenylenediaminogossypol. The latter investigators suggested that the compound which Karrer and Tobler reported to be a monoamino derivative was actually a mixture of the diamino derivative with unreacted *o*-phenylenediamine. This interpretation seems unlikely in view of the high melting point of the compound reported by Karrer and Tobler.

In contrast to the anilino derivatives of gossypol, diaminogossypol is very unstable and readily reverts to gossypol with the loss of ammonia when it is allowed to stand in solution at room temperature.[49]

As shown in Table 59, acetylation of dianilinogossypol has been reported to yield different products by different investigators. Adams, Price, and Dial [56] reported the formation of hexaacetoxydianilinogossypol upon treatment of dianilinogossypol with acetic anhydride in the presence of sodium acetate or pyridine. Murty and Seshadri [48] later reported the derivative (m.p. 185° C.) formed by acetylation of dianilino- or tetraanilinogossypol to be nitrogen-free hexacetoxygossypol. The latter investigators isolated acetanilide from the reaction mixture and suggested that the product analyzed by Adams, Price, and Dial contained admixed acetanilide. Although no analytical data were given in support of the statement concerning the identity of the gossypol derivative obtained by acetylation of dianilino- or tetraanilinogossypol, Murty and Seshadri

TABLE 59

Reported Acetyl Derivatives of Diamino- and Dianilinogossypol

Gossypol reactant	Gossypol product reported	M.p., °C.	Reported composition, %[a]			
			C	H	N	CH_3CO
Diamino-	Octaacetoxydiamino-[b]	282	65.11	5.40	3.61	40.8
Dianilino-	Hexaacetoxydianilino-[c]	185	69.94	5.82	2.89	28.4
Dianilino-[d]	Hexaacetoxy-[e]	185	—	—	0.0	—
Dianilino-	Tetraacetoxydianilino-[f]	217–217.5	69.33	5.83	2.37	20.7

[a] Calculated for octaacetoxydiaminogossypol, $C_{46}H_{48}O_{14}N_2$: C, 64.90; H, 5.64; N, 3.29; acetyl, 39.4.
Calculated for hexaacetoxygossypol, $C_{42}H_{42}O_{14}$: C, 65.45; H, 5.45; acetyl, 33.51.
Calculated for tetraacetoxydianilinogossypol, $C_{50}H_{48}O_{10}N_2$: C, 71.75; H, 5.74; N, 3.35; acetyl, 20.57.
Calculated for hexaacetoxydianilinogossypol, $C_{54}H_{52}O_{12}N_2$: C, 70.40; H, 5.70; N, 3.05; acetyl, 28.0.

[b] R. F. Miller and R. Adams, *J. Am. Chem. Soc.*, **59,** 1736–1738 (1937).

[c] R. Adams, C. C. Price and W. R. Dial, *J. Am. Chem. Soc.*, **60,** 2158–2160 (1938).

[d] Same product obtained by acetylation of tetraanilinogossypol.

[e] K. S. Murty and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **A16,** 141–145 (1942).

[f] C. H. Boatner, R. T. O'Connor, M. C. Curet, and C. S. Samuels, *J. Am. Chem. Soc.*, **69,** 1268–1271 (1947).

[56] R. Adams, C. C. Price, and W. R. Dial, *J. Am. Chem. Soc.*, **60,** 2158–2160 (1938).

pointed out that the anilino groups would be expected to hydrolyze under the conditions of the acetylation reaction, since it had previously been observed [35] that these groups are removed when dianilinogossypol is dissolved in warm acetic anhydride.

In a third investigation [34] of the products formed upon acetylation of dianilinogossypol, mixtures of several products were obtained from which one compound could be separated in pure condition. Analysis of this compound, m.p. 217–217.5° C., indicated it to be tetraacetoxydianilinogossypol. Of the four other solids of rather wide melting range isolated from the reaction mixture, the nitrogen contents ranged from 1.32 to 2.55% and the acetyl contents from 18.7 to 25.0%. The wide melting range of all of these fractions indicated that they were probably mixtures. On the other hand, acetyl contents of the four products showed that they contained little, if any, gossypol derivatives having more than four acetyl groups.

The variety of products reported to result from acetylation of dianilinogossypol might be attributed to its varying stability under the different conditions employed for its acetylation. It appears that under certain conditions, dianilinogossypol may be acetylated without loss of aniline to form hexaacetoxydianilinogossypol having two acetyl groups substituted on the anilino groups; [56] under slightly different conditions, the anilino groups may be removed, and before the molecule can rearrange to the more stable tetrahydroxy tautomer, the hexahydroxy tautomer may be acetylated to form hexaacetoxygossypol.[35] It appears that under still different conditions four acetyl groups are introduced, sometimes without loss of either of the anilino groups, and sometimes with the loss of one anilino group.[34] Reaction of tetraacetoxygossypol with aniline results in the loss of two acetyl groups to yield diacetoxydianilinogossypol.[34]

Methylation of dianilinogossypol has likewise been reported to yield different products by different investigators. Methylation of dianilinogossypol with dimethyl sulfate in chloroform solution in the presence of pyridine was reported by Adams, Price, and Dial [56] to yield two different products depending upon the temperature and duration of the reaction. Slow reaction at room temperature for periods of five days to one week yielded a red dimethyldianilinooxogossypol, m.p. 275–278° C. When the reaction mixture was refluxed overnight, a red dimethyldianilinogossypol, m.p. 253–258° C., was obtained. The resistance of both compounds to hydrolysis, and their low Zeisel numbers were interpreted as evidence that the methyl groups were attached to the nitrogen atoms of the anilino groups.

A single and entirely different product was obtained by Murty and Seshadri [48] by methylation of either dianilino- or tetraanilinogossypol with dimethyl sulfate and methanolic potassium hydroxide. The pale brown crystalline reaction product melting at 130° C. contained no nitro-

gen, and yielded the methoxyl values corresponding to those calculated for hexamethoxygossypol. This compound was later shown to be identical with hexamethoxygossypol obtained by direct methylation of gossypol.[53]

Reaction of dianilinogossypol with carbonyl reagents results in the loss of the two anilino groups. The di-dinitrophenylhydrazone and corresponding dioxime formed from dianilinogossypol are isomeric with the corresponding gossypol derivatives.[34] Dianilinogossypol reacts with pyridine to form an insoluble salt which is thermally unstable. Analysis indicates it to be dipyridyldianilinogossypol.[26, 27] The antioxidant activity of dianilinogossypol has been reported to be equal to that of gossypol when calculated on a molecular basis.[57]

The reactions of diaminogossypol have not been extensively investigated. Acetylation is reported to produce octaacetoxydiaminogossypol.[49] Upon reaction with 2,3-dimethylbutadiene-1,3, diaminogossypol loses two molecules of ammonia and yields an adduct identical with that formed by gossypol, which adds two molecules of 2,3-dimethylbutadiene-1,3, with the loss of two molecules of water.[58]

5. Esters of Gossypol

Gossypol is readily benzoylated by use of the Schotten-Baumann reaction. Carruth, who was the first to attempt purification of the reaction product, could not decide whether a tetra- or a pentabenzoyl derivative was formed, and suggested that the reaction resulted in partial decomposition of the gossypol molecule rather than simple substitution of the hydroxyl groups.[8] When the product of benzoylation of gossypol was reinvestigated by Adams and co-workers, the reaction product was first reported to be gossypol hexabenzoate on the basis of its carbon and hydrogen content,[50] but the analytical values were later [55] considered to agree more closely with those calculated for gossypol tetrabenzoate.

Carruth observed [8] that, although gossypol did not readily react with acetic anhydride alone, it was readily acetylated by this reagent in the presence of pyridine, concentrated sulfuric acid, or fused sodium acetate. He observed further that the same product was obtained regardless of which of these combinations was employed. The melting points, compositions, and proposed structures of different investigators who have acetylated gossypol with the afore-mentioned reagents, are shown in Table 60.

Differences in the reported compositions of the products obtained by different investigators may conceivably be attributed to differences in the gossypol treated. In the case of the colorless acetyl derivative, how-

[57] E. L. Hove and Z. Hove, *J. Biol. Chem.*, **156,** 611–621 (1944).
[58] R. Adams, B. Friedman, C. C. Price, R. C. Morris, and E. C. Kirkpatrick, *J. Am. Chem. Soc.*, **60,** 2160–2162 (1938).

TABLE 60

Acetyl Derivatives of Gossypol

Reactant	Gossypol derivative reported	M.p., °C.	Reported composition, %[a]		
			C	H	CH_3CO
Gossypol	Tetra- and pentaacetoxy-[b]	—	65.12	5.56	29.6
Gossypol (214°C.)	Hexaacetoxy- (white)[c]	276–277	65.25	5.59	32.8
Gossypol	Hexaacetoxy- (white)[d]	276–279	65.28	5.43	—
Gossypol	Hexaacetoxy- (yellow)[d]	184–186	66.69	5.96	32.9
Gossypol (182.5–183.5°C.)	Tetraacetoxy- (white)[e]	276–279	66.41	5.76	25.0
Gossypol (182.5–183.5°C.)	Hexaacetoxy- (yellow)[e]	—	—	—	31.4

[a] Calculated for tetraacetoxygossypol, $C_{38}H_{38}O_{12}$: C, 66.48; H, 5.54; acetyl, 25.07.
Calculated for pentaacetoxygossypol, $C_{40}H_{40}O_{13}$: C, 65.99; H, 5.50; acetyl, 29.54.
Calculated for hexaacetoxygossypol, $C_{42}H_{42}O_{14}$: C, 65.45; H, 5.45; acetyl, 33.51.
[b] F. E. Carruth, *J. Am. Chem. Soc.*, **40**, 647–663 (1918).
[c] E. P. Clark, *J. Biol. Chem.*, **75**, 725–739 (1927).
[d] R. F. Miller, D. J. Butterbaugh, and R. Adams, *J. Am. Chem. Soc.*, **59**, 1729–1731 (1937).
[e] C. H. Boatner, R. T. O'Connor, M. C. Curet, and C. S. Samuels, *J. Am. Chem. Soc.*, **69**, 1268–1271 (1947).

ever, it seems more probable that the apparent differences in composition were the result of the different methods of analysis employed.

Since Carruth found that his colorless acetylated gossypol constantly lost weight when dried at 100° C., he was uncertain of the reliability of his analytical data. On the basis of elementary analyses and of the weight of gossypol obtained by hydrolysis of the acetylated product, the latter appeared to be pentaacetoxygossypol. However, application of the method of Verley and Bölsing[59] (involving titration of phenolic hydroxyl groups with acetic anhydride and pyridine) indicated that acetic anhydride reacted with only four hydroxyl groups. Hence, Carruth concluded that either four or five hydroxyl groups in gossypol might be acetylated.

Upon reinvestigation of the product of acetylation of gossypol, Clark[9] interpreted his analytical data on the colorless derivative as indicating the formation of hexaacetoxygossypol. However, application of Perkin's method[60] for determining the acetyl content of *O*-acyl compounds yielded the values calculated for tetraacetoxygossypol; only by use of the more concentrated acid mixture required for hydrolysis of *N*-acyl compounds was Clark able to obtain acetyl analyses agreeing with the value calculated for hexaacetoxygossypol.

Upon repeating Clark's procedure with slight modifications, Miller, Butterbaugh, and Adams[50] were able to isolate a colorless and a yellow

[59] A. Verley and F. Bölsing, *Ber.*, **34**, 3354–3358 (1901).
[60] A. G. Perkin, *J. Chem. Soc.*, **87**, 107–110 (1905).

acetate. On the basis of its carbon and hydrogen content alone, which does not permit unequivocal differentiation between tetra- and hexaacetoxygossypol, the colorless derivative was reported to be hexaacetoxygossypol. The yellow derivative was reported to be a hexaacetyl derivative on the basis of its acetyl content, but it was not possible to obtain it in sufficiently pure condition to establish its complete formula. Based on the observed conversion of the colorless to the yellow form, these investigators suggested that the former is an intermediate product.

As the result of a fourth investigation of the acetylation of gossypol, it was proposed [34] that the colorless derivative was tetraacetoxygossypol and only the yellow compound was hexaacetoxygossypol. Conclusions as to the structures of the acetates were based on their carbon, hydrogen, and acetyl contents. The acetyl contents of the pure colorless and the crude yellow derivatives were determined by application of the micro method of Elek and Harte [61] for *O*-acyl compounds. No conditions were found for interconversion of the two forms.

During the course of the above investigation, it was observed that the analysis of pure dianilinogossypol by the same procedure indicated an apparent acetyl content of 1.7%.

These observations led Boatner, O'Connor, Curet, and Samuels [34] to conclude that, since Clark was able to obtain results indicating the presence of six acetyl groups in the colorless acetate only under the more drastic conditions required for hydrolysis of *N*-acyl compounds, the apparent presence of two additional acetyl groups probably resulted from decomposition of the gossypol molecule after removal of the four acetyl groups. These investigators observed further that hexaacetoxygossypol did not react with aniline, whereas tetraacetoxygossypol formed diacetoxydianilinogossypol. Consequently, it was concluded that gossypol exists in solution in two tautomeric modifications: a yellow hexahydroxy and a colorless tetrahydroxydicarbonyl form.

Gil'tburg [62] prepared a palmitate of gossypol by reaction of palmitoyl chloride and gossypol. On the basis of carbon, hydrogen, and molecular weight determinations, the compound (m.p. 40–42° C.) was reported to be hexapalmitoxygossypol.

The derivative formed upon oxidation of the colorless acetyl derivative will be discussed in later sections.

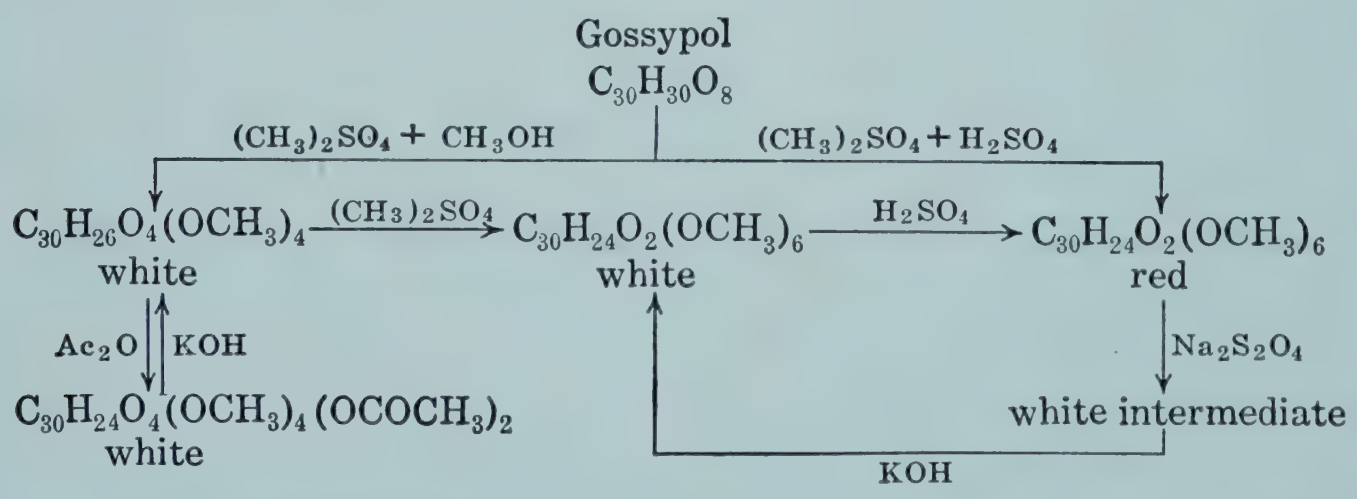
6. Ethers of Gossypol

Most of the degradation reactions normally used for determining the structure of complex organic compounds are of limited utility when

[61] A. Elek and R. A. Harte, *Ind. Eng. Chem., Anal. Ed.*, **8,** 267–269 (1936).
[62] V. E. Gil'tburg, *Masloboino Zhirovoe Delo,* **12,** 546–547 (1936); *Chem. Abst.*, **31,** 5194 (1937); *Chem. Zentr.,* **II,** 690 (1937).

applied to unsubstituted gossypol because of the instability of this pigment. This is particularly true when alkalies are present. Because the phenol groups are protected, the esters and ethers of gossypol and gossypol derivatives are much more stable than gossypol, and they have proven very useful for the preparation of partial degradation products capable of identification. The ethers are more stable to hydrolysis than the esters; consequently, the former have been investigated more thoroughly than the latter. The melting points, compositions, and proposed structures of most of the methyl ethers of gossypol which have been reported are assembled in Table 61.

Adams and co-workers, who first succeeded in methylating gossypol, reported the formation of a large number of reaction products. In the first communication on the gossypol ethers, Morris and Adams [51] recorded two, presumably dimorphic, forms of the tetramethyl ether, m.p. 190° and 259–260° C., and three forms of the hexamethyl ether, consisting of two colorless dimorphs, m.p. 221° and 235–237° C., and a red form, m.p. 158–160° C., which they considered isomeric with the colorless forms. The tetramethyl ethers were obtained by successive treatments of a methanolic solution of gossypol with dimethyl sulfate and methanolic potassium hydroxide. The red hexamethoxygossypol was obtained by the methylation of gossypol dissolved in concentrated sulfuric acid. It was also formed, along with tetramethoxygossypol, by treating a solution of gossypol in dimethyl sulfate with methanolic potassium hydroxide. The colorless hexamethyl ethers were obtained either by further methylation of tetramethoxygossypol or by isomerization of red hexamethoxygossypol. The interrelations of some of this first group of gossypol ethers were shown as in the following scheme:



In a subsequent article, Adams and Geissman [52] reported that tetramethoxygossypol was demethylated to gossypol upon treatment with concentrated sulfuric acid in acetic acid. Under the same conditions, the previously reported forms of hexamethoxygossypol were partially demethylated to dimethoxygossypol. Remethylation of dimethoxygossypol yielded a colorless hexamethoxygossypol capable of existing in three poly-

morphic forms melting at 211°, 221–223°, and 173° C., depending upon the solvents employed for recrystallization. In the same article it was reported that methylation of gossypol-acetic acid in dimethyl sulfate and methanol at 10–15° C. yielded a tetramethoxygossypol which was

TABLE 61

Methyl Ethers of Gossypol

Reactant	M.p.,°C.	Reported structure of product	M.p.,°C.	Composition, %[a]		
				C	H	CH_3O
Gossypol	214	Tetramethoxygossypol[b]	190[c]	71.15	6.70	—
Gossypol	214	Tetramethoxygossypol[b,d]	259–260	70.80	6.90	—
Gossypol	214	Hexamethoxygossypol[b]	158–160[e]	71.93	6.83	—
Gossypol	188	Hexamethoxygossypol[f]	130	71.9	7.0	30.5
Gossypol-acetic acid	—	Tetramethoxygossypol[g]	*ca.* 165	—	—	—
Hexaacetoxygossypol	276–279	Hexamethoxygossypol[f]	130	72.0	7.1	30.5
Dimethoxygossypol	191–193	Hexamethoxygossypol[h]	173[i]	71.85	6.93	32.6[j]
Tetramethoxygossypol	259–260	Hexamethoxygossypol[b]	221[h]	71.42	7.05	—
Tetramethoxygossypol	259–260	Hexamethoxygossypol[b]	235–237[e,k]	71.67	6.94	[l]
Tetramethoxygossypol	*ca.* 165	Hexamethoxygossypol[g]	175	—	—	—
Tetramethoxygossypol	[m]	Hexamethoxygossypol[h]	238–240[n]	—	—	—
Tetramethoxygossypol	[m]	Hexamethoxygossypol[h]	224–225[o]	—	—	—
Hexamethoxygossypol	238–240	Dimethoxygossypol[h]	191–193	69.96	6.01	—
Hexamethoxygossypol	130	Dimethoxygossypol[f]	[p]	—	—	—

[a] Calculated compositions of proposed methoxyl derivatives are as follows. For dimethoxygossypol, $C_{30}H_{28}O_6(OCH_3)_2$: C, 70.33; H, 6.23: CH_3O, 11.36; mol. wt., 546. For tetramethoxygossypol, $C_{30}H_{26}O_4(OCH_3)_4$: C, 71.10; H, 6.62; CH_3O, 21.62; mol. wt., 574. For hexamethoxygossypol, $C_{30}H_{24}O_2(OCH_3)_6$: C, 71.59; H, 6.98; CH_3O, 30.9; mol. wt., 602.

[b] R. C. Morris and R. Adams, *J. Am. Chem. Soc.*, **59**, 1731–1735 (1937).

[c] When heated above m.p., resolidifies and changes to a form with m.p. 259–260°C.

[d] Molecular weight (Rast), 557.

[e] Red hexamethyl ether, m.p. 158–160°C., was converted to colorless form, m.p. 235–237°C., by successive treatment with sodium hydrosulfite and methanolic potassium hydroxide; conversion was reversed by addition of excess 25% aqueous sodium hydroxide to solution in concentrated sulfuric acid.

[f] K. S. Murty and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **A16**, 146–150 (1942).

[g] R. Adams, T. A. Geissman, and R. C. Morris, *J. Am. Chem. Soc.*, **60**, 2967–2970 (1938).

[h] R. Adams and T. A. Geissman, *J. Am. Chem. Soc.*, **60**, 2163–2165 (1938).

[i] Needles from ligroin (b.p. 90–100°) or from acetone–water: m.p. 173°C. when heated rapidly; m.p. 223°C. when heated slowly. Recrystallization from acetone–methanol gave small prisms, m.p. 221–223°C.

[j] Molecular weight (Rast), 620.

[k] Colorless hexamethyl ethers melting at 221° and at 235–237°C. are reported[b] to be interconvertible by crystallization from the proper solvents.

[l] Reported molecular weight (Rast), 573.

[m] Tetramethoxygossypol not purified; crude preparation used for further methylation to hexamethoxygossypol.

[n] Recrystallized from acetone–methanol, m.p. 238–240°C.; from petroleum naphtha (b.p. 90–100°), m.p. 239–241°C.; same derivatives previously reported to have m.p. 235–237°C.[b,k]

[o] Recrystallized from acetone–methanol, m.p. 224–225°C.; from petroleum naphtha (b.p. 90–100°), m.p. 221–224°C. Identical with hexamethoxygossypol, m.p. 173–223°C., prepared from dimethoxygossypol; different from hexamethoxygossypol, m.p. 240°C.

[p] Reported to be identical with dimethoxygossypol, m.p. 191–193°C., obtained by Adams and Geissman.[h]

further methylated to form a hexamethoxygossypol melting at 238–241° C. after crystallization from acetone, methanol, or petroleum naphtha (b.p. 90–110° C.). This product was reported to be identical with the hexamethoxygossypol (m.p. 235–237° C.) previously prepared,[51] but in the earlier article it had been stated that recrystallization of this form from petroleum naphtha gave a product melting at 221° C. Methylation of gossypol-acetic acid under the same conditions as described above, except that the temperature was allowed to rise to 20–25° C., yielded a tetramethoxygossypol which could be methylated further to give a hexamethoxygossypol melting at 224–225° C. after crystallization from acetone–methanol, and at 118° C. after crystallization from petroleum naphtha (b.p. 90–110° C.).

In another article, Adams, Geissman, and Morris [63] reported another form of hexamethoxygossypol obtained by a similar two-stage methylation of gossypol-acetic acid, which melted at 175° C. when recrystallized from petroleum naphtha.

Murty and Seshadri,[53] contrary to the experience of Adams, Morris, and Geissman, found that gossypol is easily methylated by mild reagents, such as diazomethane and methyl iodide, as well as by dimethyl sulfate. Under a variety of conditions and with any of the afore-mentioned methylating agents, Murty and Seshadri obtained a single pale yellow crystalline compound melting at 130° C. Analysis of the product showed it to be hexamethoxygossypol. Methylation of colorless hexaacetoxygossypol likewise yielded hexamethoxygossypol, m.p. 130° C. When dissolved in acetic acid and treated with a little concentrated sulfuric acid, hexamethoxygossypol was partially demethylated to dimethoxygossypol, identical with that obtained by Adams and Geissman.[52]

Murty and Seshadri [53] explained the discrepancies in the properties of the various methyl ethers reported by Adams and co-workers as being due to incomplete methylation or inadequate purification. They pointed out that, with a single exception, structures were assigned to the methoxyl derivatives on the basis of carbon and hydrogen analyses alone, and these do not differ sufficiently with variation in methoxyl content to establish the identity of the methylation product. On the other hand, Murty and Seshadri identified their product as hexamethoxygossypol on the basis of methoxyl determinations. They pointed out further that the lower melting point of the methyl ether as compared with that of gossypol is consistent with a similar effect exhibited by the flavonol ethers as compared with the unmethylated compounds.

Another cause of the discrepancies in properties which have been reported for the various methyl ethers may lie in the different gossypols

[63] R. Adams, T. A. Geissman, and R. C. Morris, *J. Am. Chem. Soc.*, **60**, 2967–2970 (1938).

which were methylated. As the result of their first investigation of the structure of gossypol, Adams and co-workers [25] reported the three forms of gossypol, m.p. 184°, 199°, and 214° C., to be interconvertible by the use of appropriate solvents for recrystallization. They stated, however, that after their early work, they were able to obtain only the highest melting form. Murty, Murty, and Seshadri,[35] on the other hand, obtained gossypol melting at 188° C., and reported that they were unable to convert it into any of the other reported forms of gossypol. Consequently, it seems probable that some of the differences in the gossypol ethers obtained by these different investigators may be attributed to structural differences in the gossypol subjected to methylation.

In addition to the methyl ethers, Morris and Adams [51] reported three forms of hexaethoxygossypol. The hexaethyl ether obtained by reaction of gossypol with diethyl sulfate and aqueous sodium hydroxide was reported to fuse at 118° C. and then melt completely at 128–132° C. after recrystallization from methanol. The product resulting from reaction of gossypol with diethyl sulfate and methanolic potassium hydroxide could be obtained in two forms. After recrystallization from acetone–methanol, hexaethoxygossypol melted at 231–232° C.; upon recrystallization from petroleum naphtha (b.p. 60–110° C.), it melted at 211–212° C.

Adams and Dial [45] have also described the preparation of several methyl ethyl ethers.

Dimethoxygossypol is reported [64] to react with aniline to form dianilinodimethoxygossypol. It forms a dioxime and a diphenylhydrazone without loss of the substituted methyl groups.[51] The hexa- and tetramethyl ethers of gossypol are very stable to hydrolysis except in acetic acid, and they react with carbonyl reagents only when dissolved in acetic acid. In this solvent, with the appropriate reagents, tetramethoxygossypol forms dimethoxygossypol dioxime and dimethoxygossypol dihydrazone, both of which are isomeric with the corresponding derivatives formed by dimethoxygossypol. Under the same conditions, hexamethoxygossypol forms tetramethoxygossypol dioxime and tetramethoxygossypol dihydrazone.

Acetylation of tetramethoxygossypol [45] yields tetramethoxydiacetoxygossypol, which is readily hydrolyzed in alkaline medium to tetramethoxygossypol.

The products obtained upon oxidation and reduction of the ethers are discussed in later sections.

7. Anhydrogossypol

Carruth observed [8] that when gossypol is heated at its melting point it loses weight corresponding to the loss of two molecules of water, with the formation of a thermally stable compound. Similar treatment of

[64] R. Adams and T. A. Geissman, *J. Am. Chem. Soc.*, **60**, 2166–2170 (1938).

gossypol-acetic acid was observed to result in the formation of the same derivative, through the loss of one molecule of acetic acid and two molecules of water. Carruth designated the intensely yellow product, m.p. 246–248° C., as *B gossypol*. He found by alkaline titration that the anhydro derivative which retained the acidic properties of gossypol had an equivalent weight of 300.

Clark [9] confirmed Carruth's observation concerning the mode of formation of the anhydro product and, on the basis of its elementary composition, proposed for it the formula, $C_{30}H_{26}O_6$. He also named the compound *anhydrogossypol*. Upon recrystallization from ether, Clark obtained this product in the form of orange-colored rods which softened and partly melted at 229–230° C., and then melted completely to a black liquid at 268° C. The physical properties of anhydrogossypol reported by Miller and Adams [49] were the same as those reported by Clark.

Miller and Adams reported that the reaction of anhydrogossypol with methyl magnesium iodide indicated the presence of only two active hydrogen atoms in the molecule, in contrast to six active hydrogen atoms previously detected in gossypol by use of the same reagent.[22] It was found that anhydrogossypol could be acetylated and methylated more readily than gossypol, but yielded products identical with those formed by gossypol. Reaction with liquid ammonia resulted in the formation of diaminogossypol without the loss of water. It was later observed [58] that anhydrogossypol formed the same adduct with 2,3-dimethylbutadiene-1,3 as did gossypol and diaminogossypol.

Adams and Kirkpatrick [65] reported that a solution of the orange-colored anhydrogossypol in absolute ethanol exhibited three sharp absorption bands between 260 and 275 mμ, and presumably none in the region from 350 to 400 mμ, in which gossypol has a broad well-defined absorption band.

8. Hydrogossypol

Schmid and Margulies [22] observed that treatment of gossypol with hydrogen in the presence of palladium black resulted in the absorption of three molecules of hydrogen per molecule of gossypol. They named the resultant colorless compound *hydrogossypol* and, on the basis of elementary analyses, assigned to it the formula $C_{30}H_{36}O_8$.

Like gossypol, hydrogossypol yields five molecules of methane upon treatment with methyl magnesium iodide in pyridine at room temperature, and a sixth molecule of methane when the reaction temperature is elevated to 80° C. It was found to form no compound with acetic acid, and to react with only one molecule of *o*-phenylenediamine, with the loss of one molecule of water. Acetylation with acetic anhydride in pyridine was reported

[65] R. Adams and E. C. Kirkpatrick, *J. Am. Chem. Soc.*, **60,** 2180–2184 (1938).

to result in the introduction of six acetyl groups. Oxidation of hydrogossypol with hydrogen peroxide in alkaline solution yielded *n*-butyric acid and a dibasic aromatic acid, $C_{25}H_{30}O_{10}$, m.p. 170° C. Among the products obtained by distillation of hydrogossypol with zinc dust, only β-isoamylnaphthalene could be identified.

9. Gossypolone Derivatives

Clark observed [66] that even by the mildest oxidizing agents the gossypol molecule is decomposed into small, and on the whole, unrecognizable fragments. However, oxidation could be controlled when the phenolic groups of gossypol were protected. Treatment of a solution of the colorless hexaacetoxygossypol in acetic acid with chromic acid resulted in the formation of a yellow compound which Clark reported [67] to be a tetraacetyl derivative of a quinone formed by the replacement of two acetyl groups with two quinone carbonyl groups and the loss of the radical, C_5H_8. On the basis of its content of carbon, hydrogen, and acetyl and its molecular weight, Clark assigned it the formula, $C_{25}H_{18}O_8(COCH_3)_4$, and the name *tetraacetyl gossypolone.*

Tetraacetyl gossypolone contains no free carboxyl or hydroxyl groups. It reacts with aniline to form tetraacetoxydianilinogossypolone. This reaction was attributed by Clark to the retention of the original carbonyl groups of gossypol.

Adams, Morris, and Kirkpatrick [68] carried out similar oxidation reactions with chromic acid and the hexamethyl and diethyltetramethyl ethers of gossypol. They obtained a quinone which they designated *gossypolone tetrametyl ether* on the assumption that it was analogous to the compound obtained by Clark by oxidation of the acetate. However, they assigned the formula, $C_{30}H_{22}O_6(OCH_3)_4$, to their product, on the basis of carbon, hydrogen, and methoxyl analyses. The reactions of the quinone ether are similar to those of the acetate; it is neutral and forms a dianilino compound.

In a later article[63] the quinoid nature of the oxidized ether was established by demonstrating that the product of reductive acetylation could be reoxidized to the original quinone ether. The absorption spectrum of the quinone was found [65] to exhibit a band in the ultraviolet region in the position, and of the general shape, characteristic of naphthoquinones.[69]

Adams and Dial[45] reported the preparation of *gossypolone tetraethyl ether* by oxidation of gossypol hexaethyl ether, and of *gossypolone diethyldimethyl ether* by oxidation of gossypol diethyltetramethyl ether.

[66] E. P. Clark, *J. Biol. Chem.*, **77,** 81–87 (1928).
[67] E. P. Clark, *J. Am. Chem. Soc.*, **51,** 1475–1478 (1929).
[68] R. Adams, R. C. Morris, and E. C. Kirkpatrick, *J. Am. Chem. Soc.*, **60,** 2170–2174 (1938).
[69] A. K. Macbeth, J. R. Price, and F. I. Winzor, *J. Chem. Soc.*, **1935,** 325–333.

10. Apogossypol and Derivatives

In an attempt to split gossypol into simpler substances of known structure, Carruth [8] heated gossypol in a concentrated aqueous solution of sodium hydroxide. He obtained a colorless polyphenol, which he designated *C gossypol,* since it resembled gossypol more closely than any other known phenol. Clark [54] prepared larger quantities of this compound, which he named *apogossypol* and whose formula he established as $C_{28}H_{30}O_6$. Since he was able to isolate two moles of formic acid for each mole of gossypol reacted, he concluded that apogossypol is formed from gossypol by the elimination of two carbonyl groups. It was later suggested by Adams and Butterbaugh [55] that two aldehyde groups are lost during the formation of apogossypol.

Although apogossypol is unstable even in the solid state, Clark found that its ethers and esters are quite stable. On the basis of molecular weight, and carbon and hydrogen determinations, in conjunction with results obtained by application of Perkin's method for the analysis of *N*-acyl compounds,[60] Clark reported the acetate to be hexaacetoxyapogossypol.[70] The methyl ether of apogossypol was reported to be hexamethoxyapogossypol on the basis of molecular weight, carbon and hydrogen content, and methoxyl values determined by application of a special modification [71] of the Zeisel micromethoxyl method.

Clark [67] found that both the ester and the ether of apogossypol could be readily oxidized to quinones by reaction with chromic acid. His analytical data indicated, however, that the two quinone derivatives differed markedly. Repetition of the reactions reported by Clark led Adams and Butterbaugh to the conclusion that the structure of the quinone nucleus is the same regardless of whether the ester or ether is oxidized. The structures proposed by these investigators, as well as the analytical data on which they based their conclusions, are shown in Table 62.

On the basis of his analytical data, including determination of the molecular weight, Clark [67] concluded that his oxidation of hexaacetoxyapogossypol resulted in the formation of a diquinone by the oxidation of two acetyl groups and the loss of C_6H_{10}. Oxidation of hexamethoxyapogossypol, on the other hand, resulted in the formation of a tetraquinone containing four quinoid carbonyl groups, which was formed without loss of carbon or hydrogen from the apogossypol nucleus.

By analogy with the oxidation product of hexamethoxyapogossypol, Adams and Butterbaugh [55] assigned the formula of the tetraacetyl derivative of a tetraquinone to the product obtained by oxidation of hexa-

[70] Perkin's method for *O*-acyl derivatives indicated a tetraacetate. See discussion in section on esters of gossypol concerning probable unsuitability of the *N*-acyl method for gossypol derivatives.

[71] E. P. Clark, *J. Am. Chem. Soc.,* **51,** 1479–1483 (1929).

acetoxyapogossypol. They stated that the analytical figures reported by Clark agreed equally well with those calculated for the formula which they proposed. As shown in Table 62, this does not hold for the experimental values for the acetyl content obtained by Clark. Adams and Butterbaugh stated, further, that the analytical results which they obtained for the product of reductive acetylation of the acetyl quinone could not be reconciled with the formula proposed by Clark. However, it appears that the formula of the product could be unequivocally established only on the basis of the acetyl content of the product; and this value was not reported.

The observed failure of tetraacetoxyapogossypolone to react with aniline was attributed by Clark to the prior loss of the two carbonyl groups of gossypol during the formation of apogossypol.

The quinoid nature of Clark's *pseudogossypolone tetramethyl ether* was confirmed by Adams and Butterbaugh by its reductive acetylation and reoxidation to the original quinone. Adams and Butterbaugh renamed

TABLE 62

Oxidation Products of Apogossypol Ethers and Esters

Reactant	Name proposed for product	Proposed formula	Mol. wt.		Composition, %					
			Calcd.	Found	Calculated			Found		
					C	H	CH_3CO	C	H	CH_3CO
Hexaacetoxy-apogossypol	Tetra-acetoxy-apogos-sypolone[a]	$C_{30}H_{28}O_{10}$	548	555[b]	65.67	5.15	31.38	65.62	5.18	29.03[c]
Hexaacetoxy-apogossypol	Tetra-acetoxy-apogos-sypolone[d]	$C_{36}H_{34}O_{12}$	658	—	65.7	5.17	24.75	—	—	—
Hexamethoxy-apogossypol	Tetra-methoxy-pseudo-gossypol-one[a]	$C_{32}H_{34}O_8$	546	569[b]	70.31	6.27	23.77	70.42	6.20	23.79
Hexamethoxy-apogossypol	Tetra-methoxy-apogos-sypolone[d]	$C_{32}H_{34}O_8$	546	538	70.31	6.27	23.77	70.25	6.27	—

[a] E. P. Clark, *J. Am. Chem. Soc.*, **51**, 1475–1478 (1929).
[b] Determined by method of K. Rast, *Ber.*, **55**, 1051–1054 (1922).
[c] Determined by method of A. G. Perkins for *N*-acyl, *J. Chem. Soc.*, **87**, 107–110 (1905).
[d] D. J. Butterbaugh and R. Adams, *J. Am. Chem. Soc.*, **60**, 2174–2180 (1938).

the compound *apogossypolone tetramethyl ether* on the assumption that it contained the same quinone nucleus as the compound obtained by oxidation of hexaacetoxyapogossypol. Further differences in the reaction products of the quinones reported by Clark will be described in the section dealing with investigations of the structure of gossypol. Additional evidence for the quinoid structure of the chromic acid oxidation products of the esters and ethers was obtained by Adams and Kirkpatrick [65] in the form of the characteristic naphthoquinone band in the ultraviolet absorption spectra of these products.

Adams and Butterbaugh [55] reported that solution of hexamethoxyapogossypol in concentrated sulfuric acid resulted in the formation of a hexamethyl ether of *desapogossypol,* with the loss of C_6H_{12} from the apogossypol nucleus. On the basis of incomplete identification of the by-product, it was tentatively postulated that the reaction consisted of the loss of two isopropyl groups. Treatment of hexamethoxydesapogossypol with chromic acid in acetic acid resulted in the formation of a tetraquinone, *tetramethoxydesapogossypolone.* The quinoid structure of this compound was established by analysis of the product of reductive acetylation, and reoxidation of the latter to the original quinone.

The subsequent demonstration of the complete structure of tetramethoxydesapogossypolone, as well as that of the aromatic acid obtained by oxidation of tetramethoxyapogossypolone with potassium permanganate, will be described in the section dealing with investigations of the structure of gossypol.

11. Investigations of Structure

(a) Introduction. Because of the complexity and variety of its reactions and the ease with which the gossypol molecule undergoes alteration—not only during laboratory manipulations, but also in natural processes occurring during the development of cottonseed and its subsequent storage and processing—the determination of structure of this pigment is of considerable scientific interest and practical importance. Although a mass of data has been accumulated indicative of the identity of the reactive groups as well as their probable position in the gossypol molecule, it has not yet been possible to establish a structural formula which will adequately explain all of the reactions of gossypol.

As the result of several years of intensive investigation of gossypol and its derivatives, Adams and co-workers postulated a structural formula for gossypol which accounted for many of its reactions.[72] Their contributions have been summarized in two excellent reviews by Haworth [73] and

[72] R. Adams, R. C. Morris, T. A. Geissman, D. J. Butterbaugh, and E. C. Kirkpatrick, *J. Am. Chem. Soc.,* **60,** 2193–2204 (1938).

[73] R. D. Haworth, *Ann. Repts. on Progress Chem., Chem. Soc., London,* **36,** 284–286 (1938).

Mayer.[14] However, the subsequent synthesis of compounds having structures closely related to that proposed for gossypol [11, 74] has demonstrated the inadequacy of this structure.

In the following pages there has been assembled a brief review of the various interpretations of experimental data which have been advanced as partial solutions of the problem of gossypol structure.

(b) Attempted Classification with Other Plant Pigments. Gossypol does not appear to belong to any of the more important groups of naturally occurring plant pigments. Marchlewski [7] obtained no evidence of glucosidic or alkoxyl linkages. Carruth [8] reported that A. G. Perkin, whose series of investigations on the cotton flower pigments resulted in their identification as flavone pigments, intended to investigate the cottonseed pigments as well, but, unfortunately, desisted at Marchlewski's request. However, in his first paper on the pigments of cotton flowers, Perkin [75] stated that gossypol is not identical with, nor does it appear to be related to, the flavone pigments. The observation that the gossypol molecule appears to contain thirty carbon atoms suggested to Carruth [8] that it might be formed by condensation and subsequent reduction of two flavone molecules, but he was unable to obtain experimental data in support of this hypothesis. According to Karrer and Tobler [10] the evidence is convincing that gossypol is neither a carotenoid nor a flavone pigment.

Campbell, Morris, and Adams [25] reported several reactions of gossypol which are characteristic of phenolic naphthoquinones. It forms with stannic chloride a stable purple-red compound, which contains tin and chlorine in the molar ratio of 1:2. The formation of such compounds is a characteristic reaction of two hydroxyl groups substituted in positions adjacent or para to each other, in a naphthoquinone nucleus.[76] The red reaction product formed by gossypol with boroacetic acid is characteristic of a hydroxyl group adjacent or alpha to a carbonyl group.[77] Hydroxyl groups in the quinone ring of naphthoquinones exhibit the pronounced acidity which is evidenced by two of the hydroxyl groups of gossypol.

Pyridine salts are formed by beta hydroxyl groups in naphthoquinones and anthraquinones, except in the case of two beta hydroxyl groups adjacent to each other, which together add only one pyridine molecule.[76] Campbell, Morris, and Adams reported the preparation of dipyridylgossypol,[25] and Royce, Harrison, and Deans reported the preparation of pentapyridyldigossypol.[27] Dianilinogossypol is insoluble in alkali, but forms a dipyridine compound.[26, 27]

However, as Adams and co-workers [72] later pointed out, most of the

[74] R. Adams and D. E. Burney, *J. Am. Chem. Soc.*, **63,** 1103–1107 (1941).
[75] A. G. Perkin, *J. Chem. Soc.*, **75,** 825–829 (1899).
[76] P. Pfeiffer, *Ann.*, **398,** 137–196 (1913).
[77] O. Dimroth, *Ann.*, **446,** 97–122 (1926).

above reactions are not confined to hydroxy quinones, but are equally characteristic of other aromatic hydroxycarbonyl compounds.

The ultraviolet absorption spectra of unoxidized gossypol derivatives do not exhibit the band which has been shown to be characteristic of naphthoquinone derivatives,[69] but this band appears in the absorption spectra of the oxidation products of the ethers and esters of gossypol and apogossypol.[65]

Karrer and Tobler [10] considered the formation of a fire-red quinoxaline of gossypol and the introduction of two hydrazone radicals into gossypol with subsequent removal of only one of them by means of the Wolff-Kishner reaction, as evidence for either an α,α'-diketone or orthoquinone structure in gossypol. They stated that the orthoquinone structure appeared to be more probable.

(c) Structure of Degradation Products. Although Clark was successful in preparing many derivatives and degradation products of gossypol which yielded much information concerning the nature and distribution of its reactive groups, he was unable to determine the complete structures of any of the aromatic degradation products. The first identification of an aromatic degradation product of gossypol was accomplished by Schmid and Margulies.[22] These investigators found that, in the presence of palladium black, gossypol added three molecules of hydrogen to form hydrogossypol, $C_{30}H_{36}O_8$; and also that distillation of hydrogossypol with zinc dust resulted in the formation of β-isoamylnaphthalene. Adams and co-workers were successful in establishing the structures of several degradation products of gossypol.

Tetramethoxydesapogossypolone. The most complex of the degradation products for which Adams and co-workers established the structure by synthesis was tetramethoxydesapogossypolone. This compound is obtained from gossypol by the following series of reactions: [54, 55, 67]

$$\text{sodium gossypolate} \xrightarrow[\text{in 40\% aq. NaOH}]{\text{heated at 100° C.}} \text{apogossypol} \xrightarrow[\text{aq. NaOH}]{(CH_3)_2SO_4} \text{hexamethoxyapogossypol} \xrightarrow[\text{at room temp.}]{\text{conc. } H_2SO_4} \text{hexamethoxydesapogossypol} \xrightarrow[\text{glac. HOAc}]{CrO_3 \text{ in}} \text{tetramethoxydesapogossypolone}$$

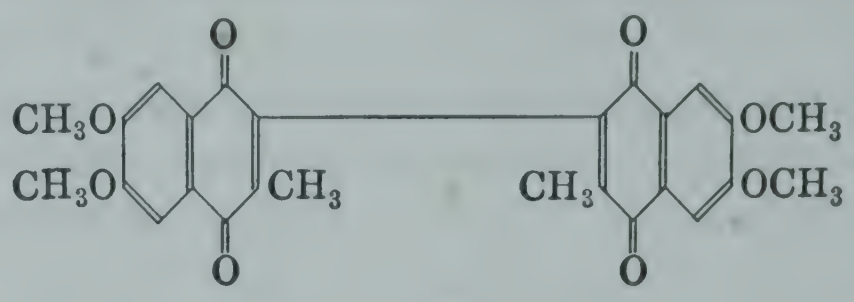
By means of a series of syntheses of compounds of known structure, Adams and Baker [78] demonstrated the structure of tetramethoxydesapogossypolone (formula I).

Desapogossypolic Acid. The acid formed by oxidation of tetrameth-

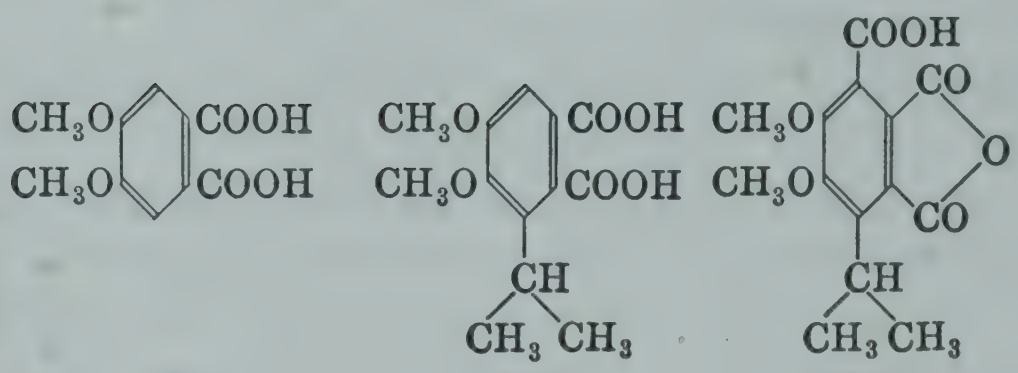
[78] R. Adams and B. R. Baker, *J. Am. Chem. Soc.*, **63,** 535–537 (1941).

oxydesapogossypolone with potassium permanganate had previously been shown [55] to be *m*-hemipinic acid (4,5-dimethoxyphthalic acid) (II).

Apogossypolic Acid. The constitution of apogossypolic acid, obtained by oxidation of hexamethoxyapogossypol with potassium permanganate in acetone,[20, 55] was shown to be [79] 3-isopropyl-4,5-dimethoxyphthalic acid (See III).



(I)

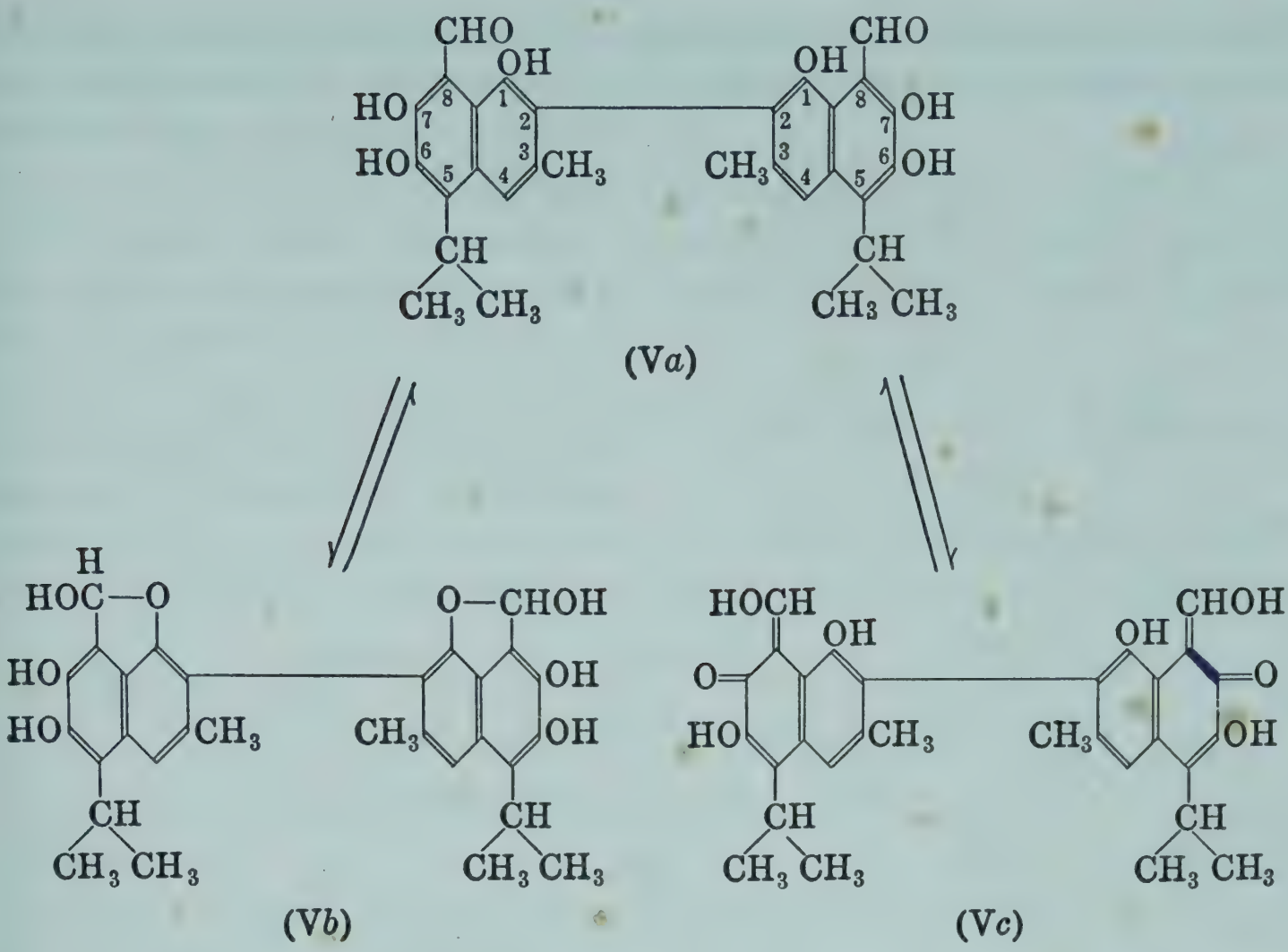


(II) (III) (IV)

Gossic Acid. It had previously been shown [80] that gossic acid, obtained by oxidation of hexamethoxygossypol with potassium permanganate,[68] is an anhydride of a tribasic acid which is decarboxylated to apogossypolic acid. Gossic acid was therefore presumed to be [79] 4-isopropyl-5,6-dimethoxyanhydrohemimellitic acid (IV).

(d) Gossypol Structure Postulated by Adams and Co-workers. *Tautomeric Forms of Gossypol.* Even before the synthesis and proof of structure of these degradation products of gossypol, Adams and co-workers [72] had proposed a structural formula for gossypol on the basis of the large number of derivatives they had investigated. Their investigations led them to the conclusion that gossypol is 2,2′-bi-1,6,7-trihydroxy-3-methyl-5-isopropyl-8-aldehydonaphthyl, which is capable of existing in the 3 tautomeric modifications shown in the accompanying formulas. According to these investigators, the hydroxy aldehyde tautomer (V*a*) is responsible for most of the normal aldehyde reactions of gossypol; the formation and reaction of the lactol tautomer (V*b*) accounts for the unusual stability of the ethers and esters of gossypol; and the cyclic carbonyl tautomer (V*c*) accounts for the diene adducts formed by gossypol, anhydrogossypol, and diaminogossypol. They were able to explain the formation and behavior of most of the derivatives which Adams and his co-workers had investigated by showing that they were derived from

[79] R. Adams and B. R. Baker, *J. Am. Chem. Soc.*, **61,** 1138–1142 (1939).
[80] R. Adams and R. C. Morris, *J. Am. Chem. Soc.*, **60,** 2188–2190 (1938).

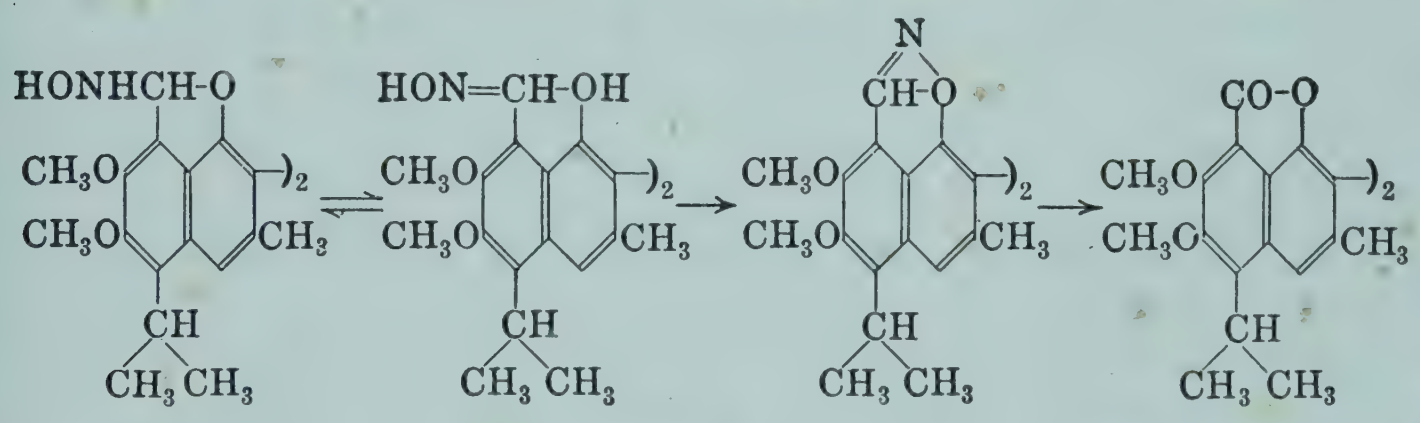


(V*a*)

(V*b*) (V*c*)

one or more of the three tautomeric structures proposed for gossypol.

Oxime Derivatives. The structure of the dioxime obtained by reaction of hexamethoxygossypol, with the loss of two methoxyl groups, was assumed to be a tautomeric mixture of two forms corresponding to formulas V*a* and V*b* of gossypol. The loss of water, followed by formation of a lactone by reaction with alkali was represented to occur as indicated in

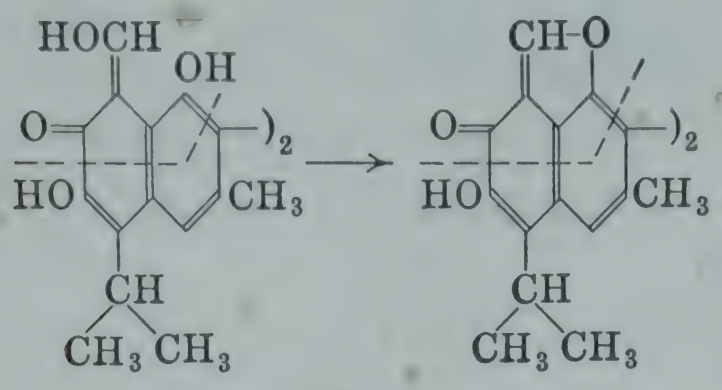


(VI)

formulas VI. Presumably the dioxime formed by gossypol would have a structure very similar to that formed by the ether, although its reactions would be more complex because of the proximity of additional free hydroxyl groups.

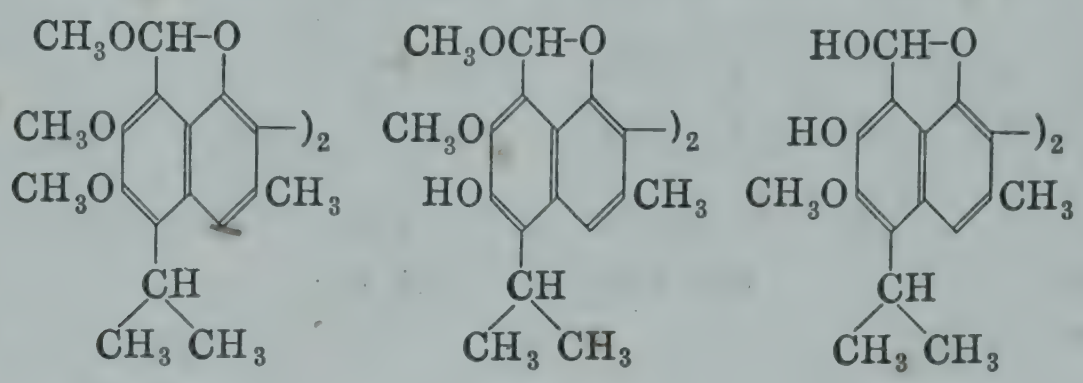
Anhydrogossypol. The observation that the products formed by gossypol and anhydrogossypol, particularly the butadiene adducts, were identical served to indicate that anhydrogossypol is formed by the elimination of two molecules of water from form V*c* of gossypol, as shown in VII.

The conjugated double bond systems (see broken lines) in the part of the molecule presumed to be involved in the reaction with butadiene are entirely analogous in the two compounds.



(VII)

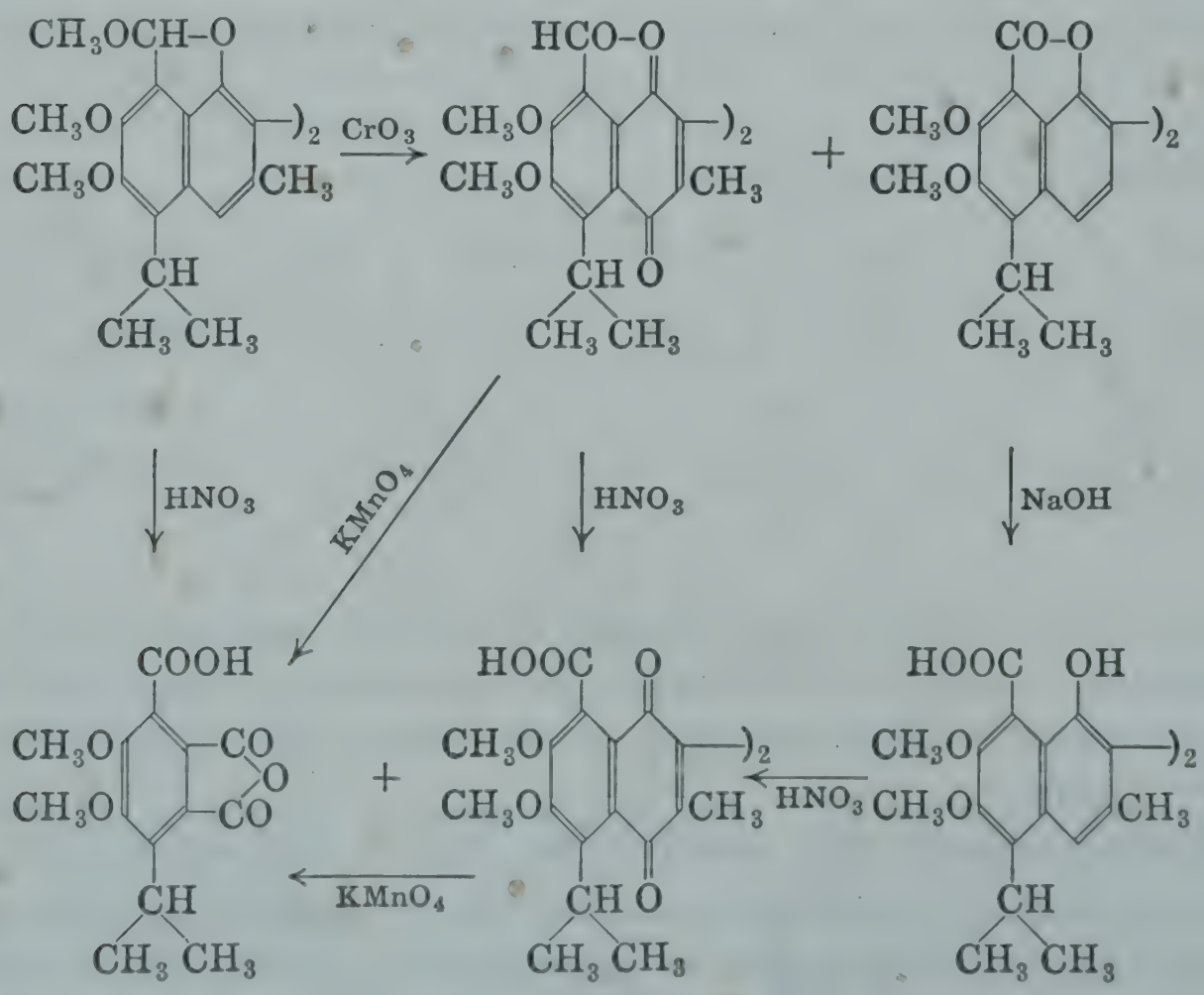
Gossypol Ethers and Esters. The reactions and interrelations of the ethers of gossypol indicated that they were derivatives of form V*b* of gossypol, and were presumed to have the forms indicated by formulas VIII (*a*, hexamethoxygossypol; *b*, tetramethoxygossypol; *c*, dimethoxygossypol). The structure proposed for hexaacetoxygossypol is entirely



(VIII*a*) (VIII*b*) (VIII*c*)

analogous to that of the corresponding ether. No structure was proposed for the yellow form of hexaacetoxygossypol, since it had not been obtained in pure form.

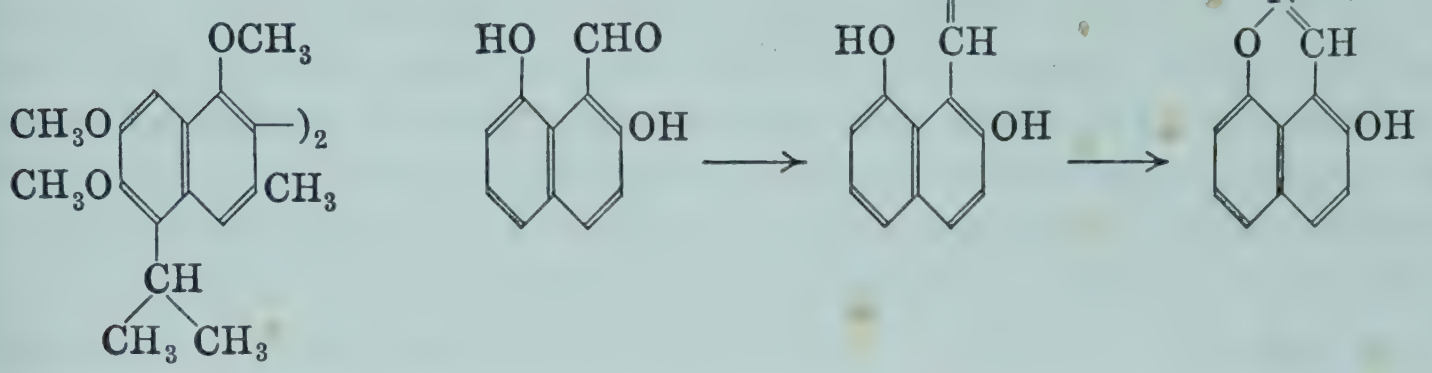
Oxidative Degradation of Ethers. The oxidative degradation of hexa-



(IX)

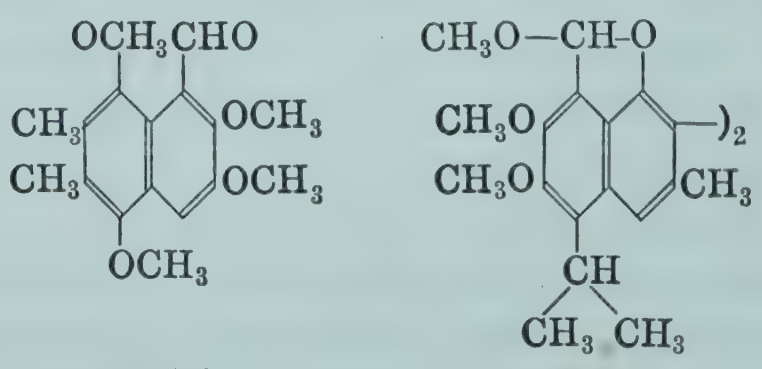
methoxygossypol resulting from its reaction with chromic acid, nitric acid, or neutral potassium permanganate to yield gossic acid as the final product was postulated to occur as shown in IX.

Hexamethoxyapogossypol. It was deduced that apogossypol is formed by elimination of the two aldehyde groups from the tautomeric form V*a* of gossypol, which would lead to structure X for hexamethoxyapogossypol.



(X) (XI)

Synthesis of Naphthaldehyde Derivatives. As pointed out by Adams and co-workers,[72] the tautomeric structures proposed for gossypol were necessarily tentative since hydroxyl and aldehyde groups in benzene compounds of corresponding structure do not behave in the manner postulated for these groups in gossypol, and no naphthalene compound of similar structure had been synthesized. Later, Adams and Burney [74] reported the synthesis of 2,8-dihydroxy-1-naphthaldehyde having the structure and forming the oxime shown in XI. This aldehyde contains all of the elements of the gossypol molecule which had been postulated to be directly involved in its tautomerism. Consequently, it was expected that it would exhibit the properties characteristic of gossypol. However, Adams and Burney found that it forms derivatives with carbonyl reagents which, in contrast to the reactions of gossypol and dimethoxygossypol, are best explained on the basis of a normal aldehyde structure. It was concluded that additional substituents, probably an additional hydroxyl group in the 3-position in the naphthalene nucleus, would be required in order to obtain a compound exhibiting the tautomerism characteristic of gossypol.



(XII*a*) (XII*b*)

More recently, Adams and Wicks [11] reported the synthesis of 2,3,5.8-tetramethoxy-6,7-dimethyl-1-naphthaldehyde (XII*a*). This compound has

all of the reactive groups postulated for gossypol,[72] and is structurally related to hexamethoxygossypol (XII*b*), except that the methods employed for its synthesis preclude the possibility of acetal formation. Hydrolysis of the methoxyl groups should yield a phenolic aldehyde analogous to gossypol, except for an additional hydroxyl group in the 5-position, which presumably should not appreciably affect the reactions of the other substituents.

Adams and Wicks were unable to demethylate 2,3,5,8-tetramethoxy-6,7-dimethyl-1-naphthaldehyde. They reported that, even when the reaction was carried out in an atmosphere of sulfur dioxide, oxidation occurred so readily that no product could be isolated. This behavior is in contrast to that of hexamethoxygossypol, which is reported to be quite stable to most reagents, but is smoothly demethylated to form dimethoxygossypol by treatment with sulfuric acid in acetic acid solution.[52, 53] Attempted demethylation of 6,7-dimethoxy-2,3-dimethyl-1,4-naphthoquinone and of 1,4-diacetoxy-2,3-dimethyl-6,7-dimethoxynaphthalene also led to the production of reaction mixtures from which no pure product could be isolated. On the basis of these observations, it seems highly improbable that either gossypol or hexamethoxygossypol has the structure postulated for it by Adams *et al.*[72]

(e) The Basic Nucleus. The demonstration of the dinaphthalene nucleus in tetramethoxydesapogossypolone [78] does not constitute incontrovertible evidence of its existence in gossypol. Many naphthalene compounds undergo coupling to form dinaphthalene derivatives under several of the reaction conditions which were employed for the formation of tetramethoxydesapogossypolone from gossypol.[55] The frequently observed formation of dinaphthyl derivatives, during oxidation [81] or reduction [82] of various compounds containing only one naphthalene nucleus, indicates a general tendency of two naphthyl residues to undergo condensation or ring fusion to form polycyclic structures. Hence, condensation of two naphthalene nuclei might have occurred during the formation of apogossypol from gossypol, or during the oxidation of hexamethoxyapogossypol to tetramethoxyapogossypolone. In the presence of mineral acids naphthoquinones readily form quinhydrones, which are subsequently oxidized to dinaphthodiquinones.[83] Reactions of this type might have occurred during conversion of tetramethoxyapogossypolone to tetramethoxydesapogossypolone in concentrated sulfuric acid solution.

Fairly conclusive evidence for the existence of the naphthalene nucleus in gossypol appears to have been presented by the isolation of β-isoamylnaphthalene from the products of distillation of hydrogossypol with zinc

[81] G. T. Morgan and D. C. Vining, *J. Chem. Soc.*, **119,** 1707–1714 (1921).
[82] F. D. Chattaway, *J. Chem. Soc.*, **67,** 653–664 (1895).
[83] J. Stenhouse and C. E. Groves, *J. Chem. Soc.*, **33,** 415–422 (1878).

dust,[22] and the formation of phthalic acid derivatives from the oxidation of gossypol and its ethers and of apogossypol ethers.[79] Nevertheless, the evidence for the existence of side chains in the gossypol nucleus is fairly certain, and oxidation of these side chains might be expected to yield phthalic acid derivatives. Cyclization of the side chains during distillation of hydrogossypol with zinc dust might account for the naphthalene derivative obtained under these conditions. Tetramethoxydesapogossypolone is the only gossypol derivative which has been demonstrated to contain the naphthalene nucleus,[78] and it was obtained only after a series of degradation reactions under conditions known to be conducive to cyclization.

Clark's observation of the relative stability of gossypol acetate and of the corresponding ester and ether of apogossypol to oxidative decomposition with chromic acid led him to the conclusion that gossypol was an aromatic compound.[67, 84]

(f) Aliphatic Side Chains. The products obtained upon oxidation of gossypol and some of its derivatives with alkaline permanganate have yielded evidence for the existence of aliphatic side chains attached to the aromatic nucleus. From the reaction mixture obtained upon addition of potassium permanganate to a solution of gossypol in sodium hydroxide, Clark [66] isolated isobutyric, acetic, and formic acids in the proportions of 0.92, 0.85, and 0.63 mole, respectively, per mole of gossypol. Clark did not attempt to interpret the formation of acetic acid but attributed the formation of formic acid to the presence of carbonyl groups in gossypol.

Clark considered the formation of almost equivalent quantities of isobutyric acid from gossypol conclusive evidence for the existence of an isobutyl side chain, probably attached through a double bond to the aromatic nucleus of gossypol. Later, he stated [20] that, in view of the lack of evidence for unsaturation in the gossypol molecule, the isobutyric acid might be considered to have been formed by the rupture of a ring having an isopropyl group as a substituent. Clark's observations of the formation of isobutyric and acetic acid from gossypol were confirmed by Karrer and Tobler.[10]

Schmid and Margulies [22] observed that gossypol rapidly adds one molecule of hydrogen in the presence of palladium black and then adds two more molecules of hydrogen much more slowly. They interpreted the rapid addition of the first molecule of hydrogen as evidence for the existence of an aliphatic double bond in gossypol. These authors obtained β-isoamylnaphthalene upon distillation of hydrogossypol with zinc dust.

The combined observations of these investigators constitute evidence for the existence of the group, $(CH_3)_2CH{-}CH{=}CH{-}$, attached as a side chain to an aromatic nucleus in gossypol. Schmid and Margulies

[84] E. P. Clark, *Oil & Fat Ind.*, **5**, 237–242 (1928).

obtained *n*-butyric acid by oxidation of hydrogossypol with hydrogen peroxide in alkaline solution.

Clark also investigated the products obtained by a two-stage oxidation of hexaacetoxygossypol, hexaacetoxyapogossypol, and hexamethoxyapogossypol. These compounds were first oxidized with chromic acid in acetic acid solution.[67] Hexaacetoxygossypol yielded an acetylated quinone, tetraacetoxygossypolone, the basic nucleus of which Clark found to be $C_{35}H_{22}O_8$. This product corresponds to a loss of C_5H_8 from the gossypol nucleus. Hexaacetoxyapogossypol yielded an acetylated quinone, tetraacetoxygossypolone, containing the nucleus, $C_{22}H_{20}O_6$, formed by losing C_6H_{10} from the apogossypol nucleus. Hexamethoxyapogossypol was converted to an acetylated tetraquinone, tetramethoxypseudogossypolone, which was formed with no loss of carbon or hydrogen from the apogossypol nucleus. Oxidation of the last-named, tetramethoxypseudogossypolone, with neutral permanganate yielded mixtures in which Clark was able to identify only isobutyric acid.[84] However, neither tetraacetoxygossypolone nor tetraacetoxyapogossypolone yielded isobutyric acid upon similar treatment. Clark concluded from these observations that the loss of the C_5H_8 and C_6H_{10} residues during the oxidation of hexaacetoxygossypol and hexaacetoxyapogossypol was due to the rupture of a ring containing the isopropyl side chain.

Adams and Baker [79] later reported that gossic acid, obtained by stepwise oxidation of hexamethoxygossypol with chromic acid and potassium permanganate, was 4-isopropyl-5,6-dimethoxyanhydrohemimellitic acid, and that apogossypolic acid, obtained by similar treatment of hexamethoxyapogossypol, was 3-isopropyl-4,5-dimethoxyphthalic acid. On the assumption of the presence in gossypol of a naphthalene nucleus, these derivatives were considered as establishing the position of the hydroxyl, isopropyl, and aldehyde substituents in gossypol. However, the same derivatives might have resulted equally as well from the oxidation of aliphatic side chains attached to a benzene nucleus.

The abnormal methoxyl values obtained for gossypol and some of its derivatives upon prolonged refluxing with hydriodic acid were attributed by Clark [71] to decomposition of the gossypol molecule, with possible formation of formaldehyde. By analogy with the observations reported for other alkyl naphthalene compounds,[85] Adams and associates [72] attributed the abnormal methoxyl values obtained during their investigations [63] to fission of the isopropyl group from the gossypol nucleus. However, Murty, Murty, and Seshadri [35] reported that they obtained no indication of a methoxyl group in gossypol, while Murty and Seshadri [53] reported methoxyl values for hexamethoxygossypol which agreed with the calculated values.

[85] H. Meyer and K. Bernhauer, *Monatsh.*, **54**, 721–752 (1939).

By carefully controlled ozonization of gossypol, Karrer and Tobler [10] obtained oxalic acid and an aromatic *o*-hydroxycarboxylic acid which they named *gossypolic acid*. On the basis of the elementary analysis of the acid and its dimethyl ester, they established the empirical formula of gossypolic acid as $(C_{12}H_{14}O_4)_x$, but determinations of its molecular weight were inconclusive. Subsequent determination by Adams *et al.*[86] of the molecular weight of the dimethyl ester as 485 was interpreted by these investigators as evidence that gossypolic acid is a dihydroxybiphenyldicarboxylic acid. A mechanism for its formation from gossypol was proposed.

(g) Functional Groups. Gossypol undergoes many reactions which can readily be interpreted in terms of individual reactive groups characteristic of less complex organic compounds. Analysis of its readily formed esters and ethers indicates the presence in gossypol of four [8, 34] to six [9, 25, 53] hydroxyl groups. The neutral salts formed by the reaction of gossypol with strong bases constitute evidence of the presence of two strongly acidic groups. The formation of dicarbonyl derivatives is indicative of the presence of two carbonyl groups in the gossypol molecule. Moreover, gossypol undergoes a number of additional complex reactions. Although it is a strong dibasic acid, it also reacts readily with acids, but the compounds formed are quite unstable and decompose into the original reactants under the influence of heat or moisture.

Several of the reactions of gossypol, such as the formation of dicarbonyl derivatives and the ready reduction of Fehling's solution and ammoniacal silver nitrate, have been interpreted by Adams and co-workers [72] as evidence that gossypol is an aromatic hydroxy aldehyde. However, many of its reactions are not characteristic of any known aromatic hydroxy aldehyde. No coumarin-type derivatives appear to be formed by treatment of gossypol with acetic anhydride in the presence of sodium acetate, pyridine, or sulfuric acid. Gossypol reacts with methyl magnesium iodide to yield six molecules of methane, but gossypol is recovered unchanged from the hydrolyzed reaction mixture.[22] The reaction of gossypol with concentrated aqueous sodium hydroxide at elevated temperatures results in the formation of apogossypol, a polyphenol containing no carboxyl groups.[8, 54] Oxidation of hexamethoxygossypol with chromic acid yields a quinone containing no carboxyl groups.[68]

Gossypol is intramolecularly reactive owing to the possibility of interaction of various groups attached to its hydrocarbon nucleus. Completely methylated gossypol is insoluble in aqueous bases and reacts with carbonyl reagents with the loss of two methoxyl groups.[63] The fact that dianilinogossypol is no longer soluble in alkali indicates that the acidic phenol groups are involved in the formation of this derivative. On the

[86] R. Adams, T. A. Geissman, W. R. Dial, and J. T. Fitzpatrick, *J. Am. Chem. Soc.*, **63,** 2439–2441 (1941).

other hand, although dianilinogossypol is very stable under most conditions, it reacts readily with carbonyl reagents with the loss of the anilino groups under either acidic or basic conditions. The carbonyl derivatives thus obtained are isomeric with those formed by direct treatment of gossypol.[34] The lactol formed by reaction of the dioxime of dimethoxygossypol was interpreted by Adams and co-workers [72] to be the result of the interaction of the oxime group with the *peri*-hydroxyl groups of an 8-hydroxynaphthaldehyde. Moreover, although the two carbonyl groups of gossypol have usually been assumed to be alike, Karrer and Tobler [10] reported that only one hydrazone radical was removed from gossypol dihydrazone by the Wolff-Kishner reaction.

Many of the reactions of gossypol might be attributed to the presence of one of more enolizable carbonyl groups. The recovery of gossypol after reaction with methyl magnesium iodide might be explained on this basis. The change from pale yellow to intense yellow which gossypol undergoes upon solution in aqueous hydroxides could easily be attributed to enolization. Similarly, the absence of acidic properties in dianilinogossypol and the shift, during its formation from gossypol, of the absorption bands toward longer wave lengths has been attributed [34] to an increase in the number of conjugated double bonds resulting from the reaction of the enol tautomer of gossypol. The formation of the intensely yellow-colored hexaacetoxygossypol by reaction of gossypol with acetic anhydride in the presence of sodium acetate, sulfuric acid, or pyridine might likewise be attributed to enolization, since energetic treatment of aldehydes or ketones containing an alpha hydrogen atom is known to result in their acetylation.[87]

12. Absorption Spectra of Gossypol and Gossypol Derivatives

(a) Application of Spectrophotometry. With the development of commercial photoelectric instruments, spectrophotometry has become a most exact and readily available analytical procedure. With the use of very small quantities of material, the complete absorption spectrum of a complex organic compound can be determined within a comparatively short period of time, throughout the visible and ultraviolet wave length region with a high degree of accuracy. The relative ease and extreme accuracy with which such measurements can be made have resulted in the increased application of spectrophotometric methods. Unfortunately, the theoretical limitations of absorption spectra methods for the establishment of the structure or the identity of complex organic compounds are not always fully appreciated by investigators employing these methods.

The theory which relates absorption spectra and molecular structure may be briefly summarized as follows. Molecules absorb electromagnetic

[87] F. W. Semmler, *Ber.*, **42,** 548–591, 1161–1163 (1909).

vibrations of frequencies corresponding to their own frequencies of vibration. Absorption in the visible and ultraviolet wave length regions is the result of electronic vibrations in the molecule; that in the infrared corresponds to atomic and molecular vibrations and rotations.

In the visible and ultraviolet regions, complex organic molecules possess a number of characteristic electronic vibrational frequencies which result in the phenomenon of selective absorption, *i.e.*, absorption of light in more or less widely separated bands. Each part of the molecule may have a characteristic vibrational frequency of its own, but the vibration of a given group may in turn be modified by the presence of other groups, so that the over-all intramolecular vibrations of a combination of resonators may be cumulative, conjugated, or separated.

Spectral absorption may therefore be considered as a highly constitutive molecular property. With few exceptions, the effect on the resonance and hence absorption spectrum resulting from the introduction into a given molecule of specific groups cannot be predicted with any degree of accuracy. Seemingly slight modifications in molecular structure may produce marked changes in absorption spectrum; on the other hand, the introduction of substituents which profoundly affect other physical and chemical properties of a compound may produce little or no change in either the location or the intensity of its characteristic absorption bands. Absorption spectra data are, therefore, of only limited utility in establishing the molecular structure of a compound unless supplemented by other physical and chemical data.

On the other hand, the characteristics of absorption spectra which limit their applicability to the determination of molecular structure constitute their principal advantage for identification purposes. Because of the highly constitutive nature of absorption phenomena, if the absorption spectra of two compounds exhibit identical extinction coefficients throughout a wide wave length range, it may be safely concluded that the compounds are structurally closely related. If two compounds are isolated from the same natural source, and possess identical absorption spectra, as well as similarity in other physical and chemical properties, it may be presumed that the compounds are identical. The application of spectrophotometry to the identification of naturally occurring pigments, such as gossypol and related products, is particularly advantageous, since these compounds usually exhibit characteristic absorption in both the visible and ultraviolet regions.

Since instruments for the direct measurement of absorption spectra in the infrared region have only recently become commercially available, the field of infrared spectrophotometry has to a large extent remained in the hands of specialists. Absorption in the infrared is the result of the interaction or resonance of atomic and molecular vibrations and rota-

tions. Although the infrared absorption spectrum of a given organic molecule often appears more complex than its ultraviolet and visible absorption spectrum, it is also frequently capable of yielding more conclusive information concerning the presence or absence of certain reactive groups. For example, the rotation-vibration frequencies associated with carbonyl, hydroxyl, and other groups in the infrared region are not significantly affected by the presence of other groups. Consequently, the presence of such groups in complex organic molecules is readily detected by means of infrared absorption spectra.

(b) Absorption Spectra of Gossypol in the Ultraviolet and Visible Regions. It has been demonstrated [29] that the absorption spectra of solutions of gossypol in chloroform or ethanol change with the age of the solution; and that the change occurs more rapidly in ethanol than in chloroform. Consequently, spectrophotometric analyses intended to establish the purity of gossypol preparations should always be determined with freshly prepared solutions, and preferably in chloroform. Moreover, since it has been established that high temperatures effect alteration of the gossypol molecule, the final operations involved in the purification of gossypol should always be carried out at low temperatures. By observing these precautions, it has

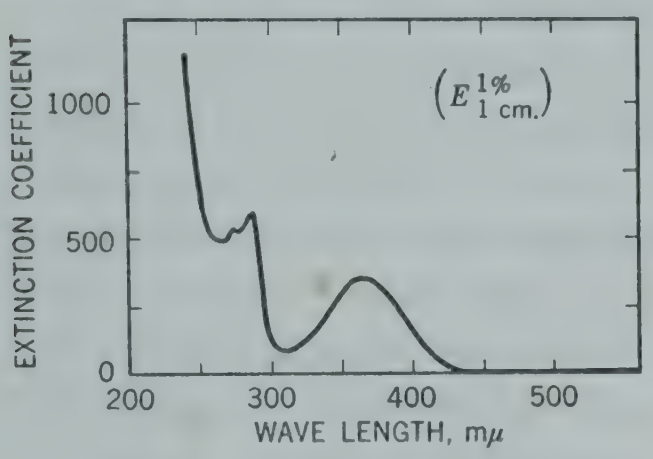


Fig. 42. Absorption spectrum of pure gossypol, m.p. 184° C., in chloroform.[34]

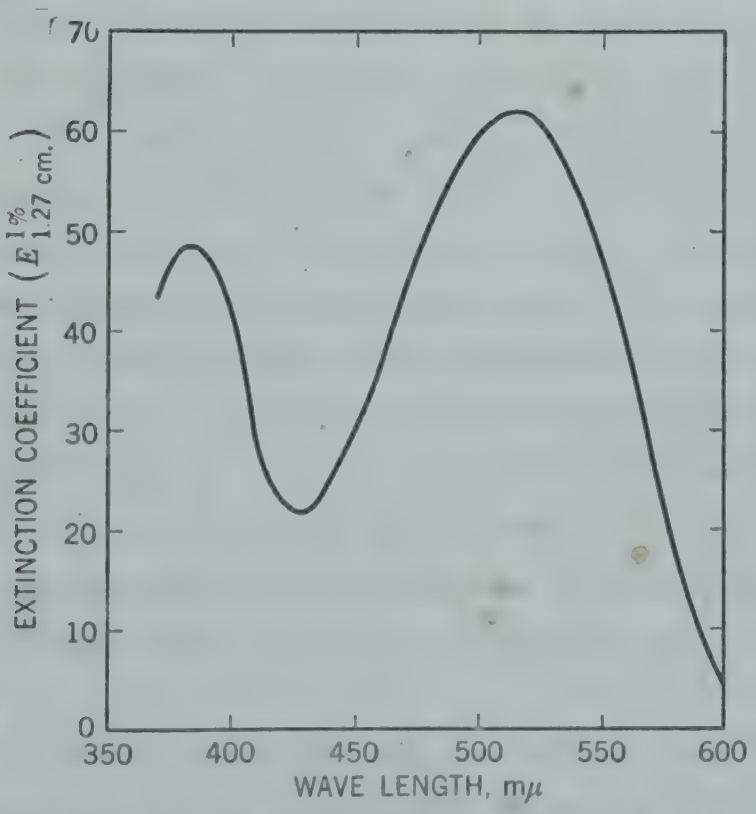


Fig. 43. Absorption spectrum of the product of the gossypol–antimony trichloride reaction.[46]

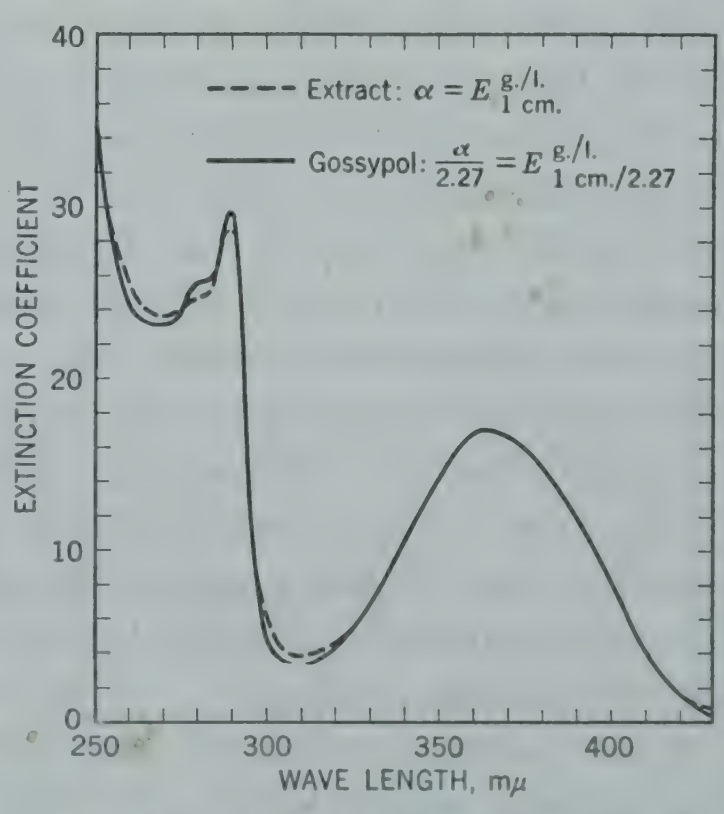


Fig. 44. Absorption spectrum of chloroform extract of cottonseed pigment glands and pure gossypol in the extract.[39]

been possible to obtain gossypol [29, 34] from different samples of cottonseed whose chloroform solutions exhibit the common absorption spectrum shown in Figure 42. The values of the specific extinction coefficients of those preparations of gossypol (1, 2, and 3 in Table 63) at points of maximum and minimum absorption agree with each other within the limits of experimental error.

In addition to the characteristic absorption of its solutions in various organic solvents, gossypol forms with antimony trichloride a stable reaction product whose chloroform solution also exhibits characteristic absorption in the near ultraviolet and visible regions.[46] As may be seen in Figure 43, the absorption spectrum of the gossypol–antimony trichloride reaction product exhibits two broad absorption bands, with maxima at 380 and 520 mμ, and a minimum at 430 mμ. Within a relatively wide range of concentration, the specific extinction coefficients at the absorption maxima are directly proportional to the concentration of gossypol. Thus, the absorption spectrum of the gossypol–antimony trichloride reaction product may serve as an additional criterion for establishing the purity of any given preparation of gossypol.

The values of the specific extinction coefficients of the antimony trichloride reaction products formed by the first four gossypol preparations shown in Table 63 range from 62.9 to 67.0.

TABLE 63

Specific Extinction Coefficients of Chloroform Solutions of Various Preparations of Gossypol

Sample	Minimum at 263–271 mμ	Maximum at 276–279 mμ	Minimum at 282 mμ	Maximum at 288–289 mμ	Minimum at 309–310 mμ	Maximum at 362–366 mμ
1[a]	476	502	512	601	73.0	348
2[b]	488	530	520	610	72.7	352
3[a]	465	505	498	584	72.8	342
4[c]	529	579	569	674	77.4	386
5[d]	547	594	588	686	82.9	397

[a] Isolated as sodium gossypolate from an ethereal extract of cottonseed; gossypol recrystallized from ether – petroleum naphtha at 3.3°C.

[b] Isolated as gossypol-acetic acid from an ethereal extract of defatted cottonseed; gossypol recrystallized from ether – petroleum naphtha at 3.3°C.

[c] Same source as Sample 3; ethereal solution of pure gossypol-acetic acid heated in contact with hot water.

[d] Sample furnished by F. H. Smith; ethereal solution of pure gossypol-acetic acid heated in contact with hot water.

Comparison of Isolated Gossypol with the Naturally Occurring Pigment. Gossypol has been shown [39] to be a major component of the pigment glands of cottonseed. It was also shown [42] that contact with ether, chloroform, or aqueous ethanol extracts all of the gossypol from these

organs. For purposes of comparison, the material extracted by ether or aqueous ethanol was transferred to chloroform. The absorption spectra of extracts obtained from a series of samples of pigment glands, of which a typical example is shown in Figure 44, were observed to be very similar and to resemble closely the absorption spectrum of pure gossypol in chloroform.

For a more accurate comparison, the gossypol contents of the extracts were determined by the antimony trichloride spectrophotometric method,[46] and the extinction coefficients were calculated for the absorption due to the presence of gossypol in the extracts. The curves constructed from these calculated values, of which a typical example is shown in Figure 44, were identical with the experimentally determined curves of the corresponding gland extracts.

These investigations have demonstrated that the structure of gossypol is not permanently altered by reaction with the reagents, aqueous alkali and acetic acid, utilized for its separation from extracts of cottonseed. Experimental data have not yet been obtained to determine whether gossypol suffers alteration during its extraction from cottonseed. Consequently, the state in which gossypol occurs in the pigment glands is not yet known. It seems probable that gossypol is dissolved in the other gland components as a colloidal or a true solution since the glands appear perfectly clear. However, the possibility has not been excluded that gossypol occurs in chemical combination with other components of the pigment glands.

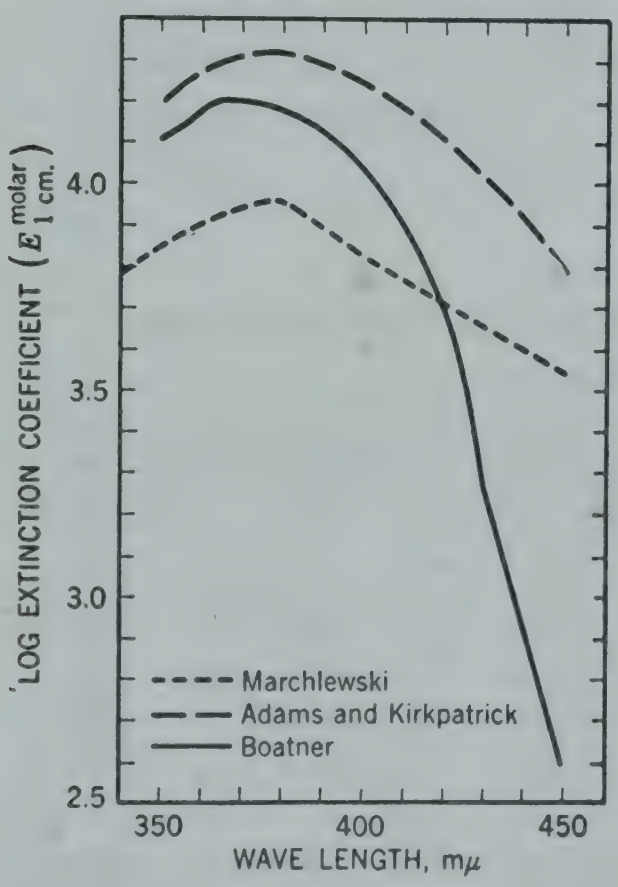


Fig. 45. Absorption spectra of ethanol solutions of gossypol reported by Marchlewski, by Adams and Kirkpatrick, and by Boatner (according to Boatner[29]).

Variations in Absorption Spectrum Attributable to Methods of Preparation. The method used for the recrystallization of gossypol, the purity and temperature of the solvent in which it is dissolved, and the age of the solution—all affect the absorption spectrum of gossypol. Comparison of the absorption spectra of ethanol solutions of gossypol (Fig. 45) which have been reported by different investigators[29, 65, 88] clearly indicates the marked differences which have been observed in the values of the extinction coefficients at the absorption maximum in the near ultraviolet region. Lack of recorded data on the methods used for the purification and the

[88] R. Grunbaumowna and L. Marchlewski, *Biochem. Z.*, **286,** 295–296 (1936).

preparation of the solutions of two of these products[65, 88] renders it impossible to suggest the cause of these differences.

The influence of elevated temperatures on the absorption spectrum during the recrystallization of gossypol has recently been reported.[34] Gossypol, melting at 182–183° C., was obtained by hydrolyzing an ethereal solution of gossypol-acetic acid with hot water and then washing the liberated gossypol with toluene. The recovered gossypol contained 68.46% carbon and 5.88% hydrogen. The values of the specific extinction coefficients of the gossypol–antimony trichloride reaction product were consistent with the values obtained with other preparations of gossypol. However, the characteristic absorption of a chloroform solution of the gossypol obtained by hydrolysis of gossypol-acetic acid in contact with hot water (Sample 4, Table 63) was more intense than that of other preparations obtained by recrystallization at a low temperature. Recrystallization of this product from ether–petroleum naphtha solution at 3.3° C. yielded gossypol with an absorption spectrum (Sample 3, Table 63) agreeing closely with that of other gossypol preparations.

The absorption spectrum (Sample 5, Table 63) of a chloroform solution of another sample of gossypol,[89] obtained by hydrolysis of an ethereal solution of pure gossypol-acetic acid in contact with hot water,[31] was likewise found to exhibit the enhanced absorption characteristic of gossypol after exposure to elevated temperatures.

Relation between Melting Point and Absorption Spectrum of Gossypol. Campbell, Morris, and Adams[25] were able to obtain gossypol exhibiting the three melting points (184°, 199°, and 214° C.) which have been reported for this compound. These investigators reported that the three forms are polymorphic. The absorption spectra of chloroform solutions of these three forms[90] are reproduced in Figure 46. The samples used were all several years old but did not appear to have decomposed. The absorption spectra of two products, melting at 214° C., were superimposable.

The ratios of the specific extinction coefficients at points of maximum and minimum absorption were essentially the same regardless of the melting point. However, significant differences in intensity of absorption were noted. The absorption exhibited by the highest melting product (214° C.) was greater than that of the intermediate product (199° C.), which was in turn greater than that of the low-melting material (184° C.).

Hence, it was concluded that differences in the melting point of gossypol were associated only with corresponding changes in the intensity of its absorption spectrum. However, the occurrence of differences in the

[89] Sample furnished by F. H. Smith.
[90] Samples furnished by R. Adams.

intensities of the bands with no concurrent shifts in their positions is an unusual phenomenon, which is difficult to explain.

Effect of Solvent and Age of the Solution on the Absorption Spectrum of Gossypol. The absorption spectrum of highly purified gossypol has

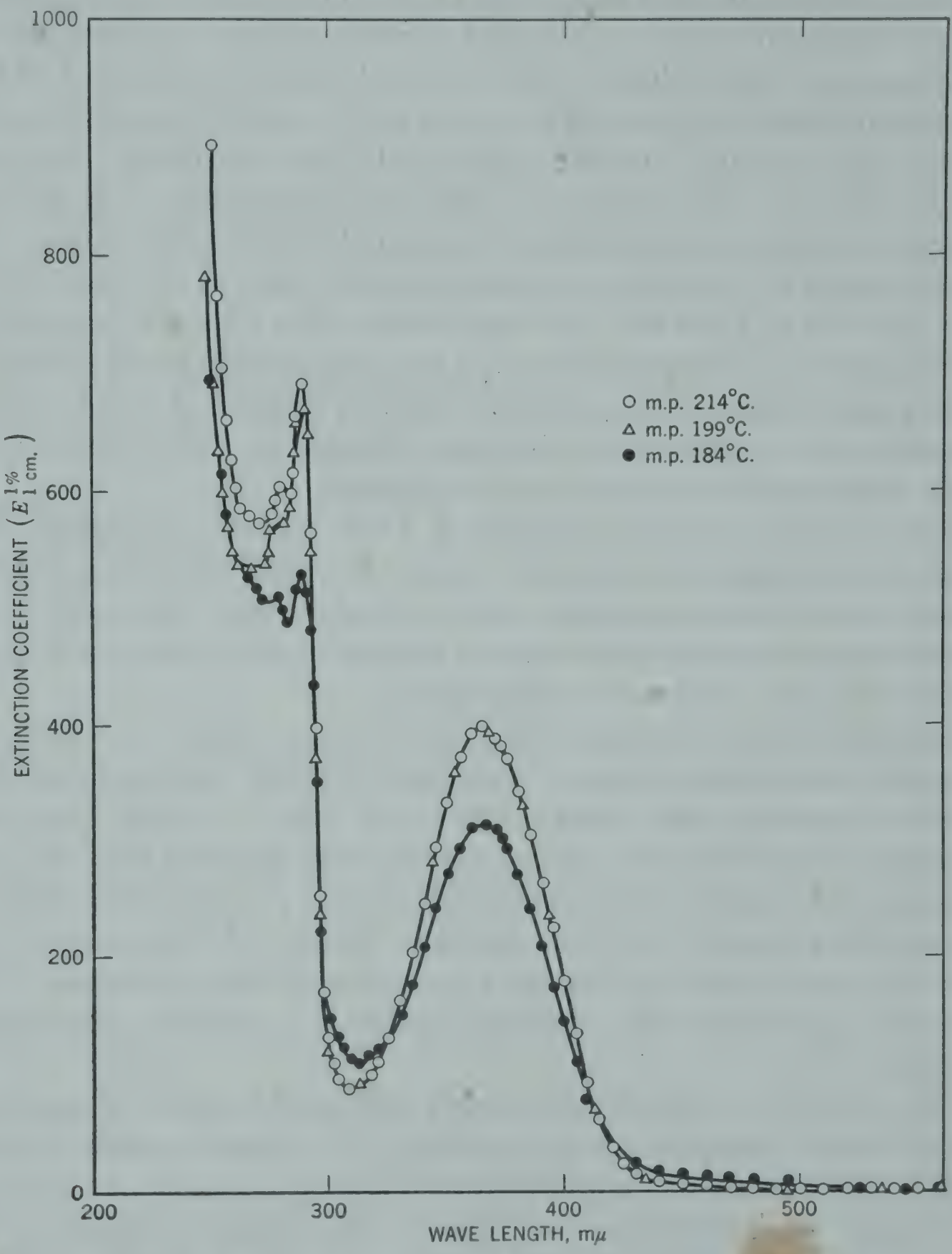


Fig. 46. Absorption spectra of chloroform solutions of different specimens of gossypol prepared by Adams and Kirkpatrick.

been determined in ethanol, chloroform, and cyclohexane as shown in Figure 47. Inspection of these curves indicates a shift in the absorption bands toward longer wave lengths and a decrease in their intensity with increasing polarity of the solvent. Part of the increased intensity of

absorption of gossypol in cyclohexane may be due to molecular rearrangement caused by the heating required to effect solution in this solvent.

Gossypol was demonstrated[29] to be unstable in solution, by spectrophotometric examination of chloroform and ethanol solutions (Figs. 48 and 49) which had aged for different lengths of time. As is evident from the heights of the absorption maxima, the absorption decreases slowly in chloroform and rapidly in ethanol solution. On the other hand, the spectral absorption of gossypol in cyclohexane increases upon standing, as may be seen by reference to Table 64.

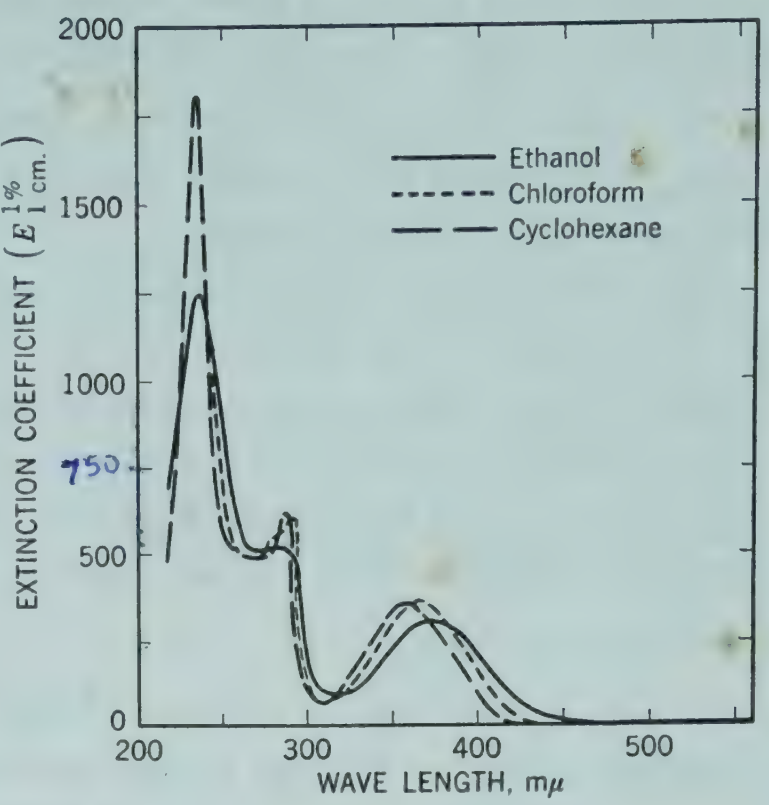


Fig. 47. Absorption spectra of solutions of gossypol.

The effect of age on chloroform solutions of gossypol may be observed in the absorption spectra of the products formed by treating such solutions with antimony trichloride. The extinction coefficient at 380 mμ remains the same, but that at 520 mμ decreases in proportion to

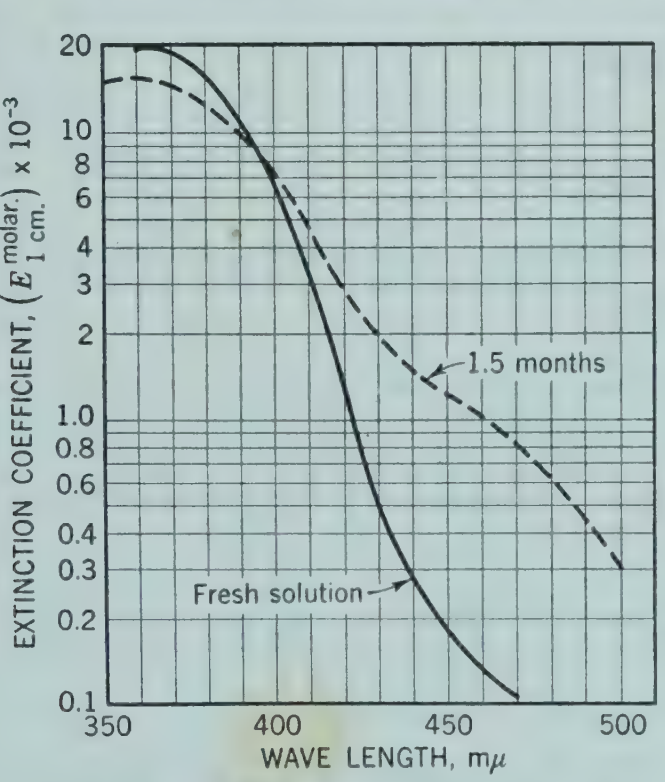


Fig. 48. Alteration in absorption spectrum of chloroform solutions of gossypol on aging.[29]

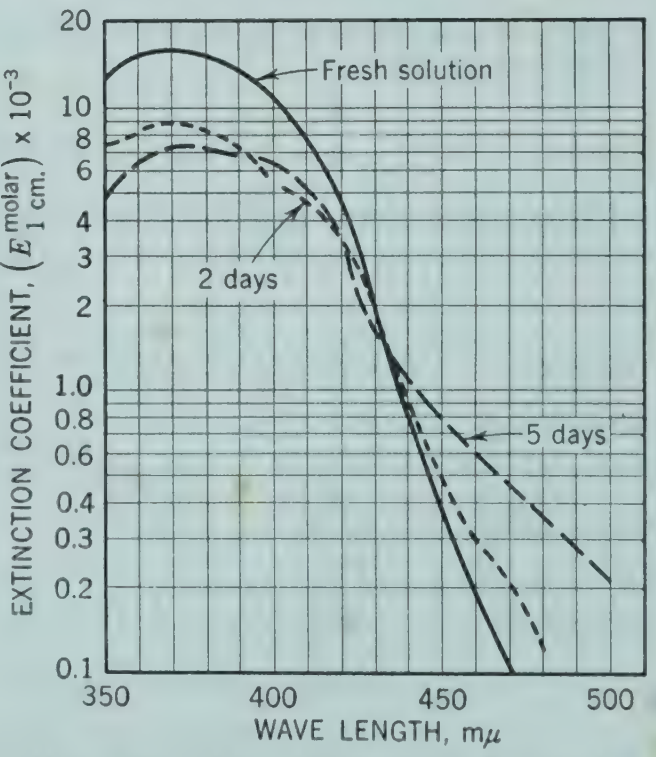


Fig. 49. Alteration in absorption spectrum of ethanol solutions of gossypol on aging.[29]

the age of the solution. The absorption band at 520 mμ is completely absent in the antimony trichloride reaction products of chloroform solutions of gossypol allowed to stand at room temperature for a year or longer.

Gossypol also undergoes alteration upon storage in the solid state. The melting points of various samples of gossypol have been found to decrease by as much as 10° C. after storage for periods of three months to three years. The extinction coefficients at 520 mμ of solutions of the antimony trichloride reaction products prepared from aged samples of gossypol have been found to decrease significantly, the decrease being greatest in the case of the oldest sample.

The elementary composition of stored samples of gossypol was found to be identical with that of freshly prepared samples; and, as shown in Table 65, the absorption spectra of chloroform solutions of these samples were identical, within the limits of experimental error, with those of pure freshly prepared gossypol. The absorption spectra of ethanol and cyclohexane solutions were also similar to those of freshly recrystallized gossypol.

TABLE 64

Effect of Age on Specific Extinction Coefficients of Cyclohexane Solutions of Gossypol

Age of solution	Maximum at 236 mμ	Maximum at 276–277 mμ	Maximum at 286 mμ	Maximum at 357–359 mμ
Fresh[a]	1697	471	577	334
29 hrs.[b]	1848	507	618	353

[a] Gentle warming necessary to obtain solution.
[b] Stored at 25°C.

TABLE 65

Effect of Age on Specific Extinction Coefficients of Chloroform Solutions of Gossypol

Sample	Minimum at 264–267 mμ	Maximum at 278–279 mμ	Minimum at 282 mμ	Maximum at 288–289 mμ	Minimum at 309–310 mμ	Maximum at 362–365 mμ
Old	487	526	516	606	77.5	349
Recrystallized	488	530	521	610	72.7	352
Old	488	524	519	602	75.4	351
Recrystallized	476	517	512	601	73.0	348

Recrystallizatoin of aged samples from mixtures of ethyl ether and petroleum naphtha resulted in the recovery of small amounts of crystalline gossypol which melted sharply at 184° C., and exhibited the absorption spectrum in chloroform (Table 65) and in ethanol and cyclohexane which are characteristic of pure gossypol. The absorption spectra of the antimony trichloride reaction products of the freshly recrystallized gossypol were identical with those obtained with other pure gossypol preparations.

The agreement in the analytical data and absorption spectra of old

and freshly recrystallized gossypol might appear to indicate the presence of only small amounts of decomposition products. However, determination of the absorption spectrum of the gossypol–antimony trichloride reaction products makes it possible to estimate accurately the concentration of gossypol,[46] and application of this method revealed significant changes in gossypol content during aging of the samples. It would appear, therefore, that the alteration in the gossypol samples upon aging represents a molecular rearrangement which can be detected only by the alteration in the intensity of the absorption band at 520 mμ of the antimony trichloride reaction product.

Deductions Concerning the Structure of Gossypol. Investigation of the absorption spectra of gossypol and several of its derivatives led Adams and Kirkpatrick[65] to the conclusion that the intensity of its absorption could be explained only by assuming the presence of aromatic rings. They reported that a comparison of the absorption spectrum of gossypol with those of substituted naphthalene derivatives indicated the former to be of the same general shape as the latter, but with subdued detail.

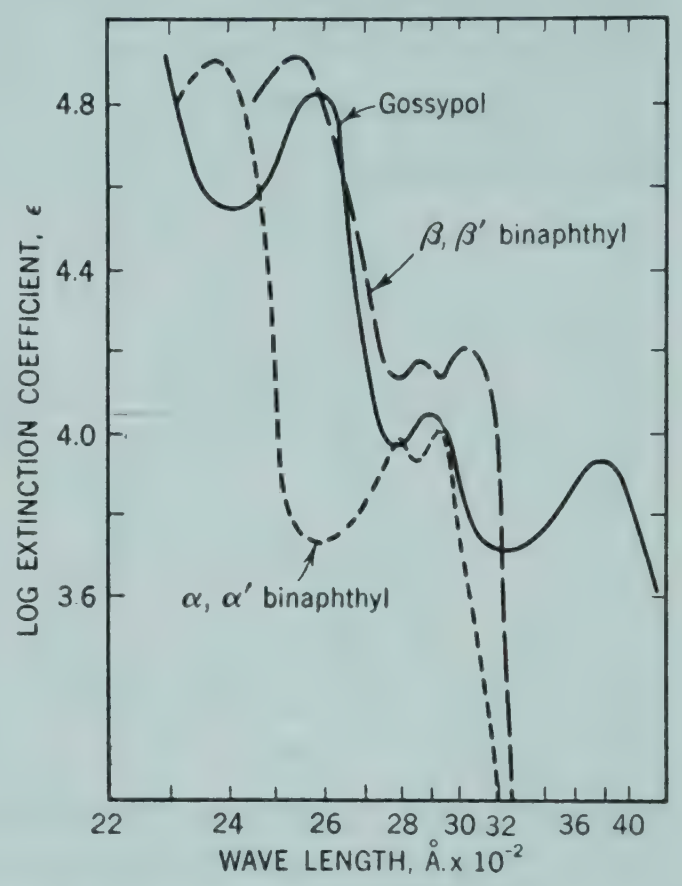


Fig. 50. Absorption spectra.[65]

These investigators found that the spectra of compounds having more complex condensed ring systems, such as phenanthrene, anthracene, chrysene, and other complex aromatic hydrocarbons, were quite different from that of gossypol. Since it appeared that the difference in the absorption spectra of gossypol and naphthalene derivatives was principally one of intensity, the absorption spectra of several dinaphthalene derivatives were determined for comparison. The difference in the absorption spectra of gossypol as compared to β,β′-binaphthyl and α,α′-binaphthyl (Figure 50) was attributed by these investigators to the presence of substituents in the gossypol molecule, and it was concluded that the basic nucleus of gossypol was probably either α,α′-binaphthyl or β,β′-binaphthyl. In view of the difference in the absorption spectra of these compounds, the conclusions of these investigators do not appear to be justified on the basis of the spectrophotometric data presented. Comparison of the spectra of gossypol in cyclohexane, chloroform, and ethanol solutions shows that in the polar solvents the absorption bands are shifted toward longer wave lengths, and their intensities are lowered. Since this phenomenon is

characteristic of compounds containing conjugated and enolizable carbonyl groups,[91] it can be concluded that the spectrophotometric data constitute confirmatory evidence for the presence of such groups in the gossypol molecule.

The absorption band at 236–237 mμ, which is exhibited by ethanol and cyclohexane solutions of gossypol, has been reported [91, 92] to be characteristic of a diene linkage. Enhancement of this band in cyclohexane may be due to either a solvent effect or alterations in the configuration of the gossypol molecule due to the heating necessary to effect solution in this solvent. Since gossypol is not soluble in cyclohexane without the application of heat, no simple means of distinguishing the two effects is readily available.

(c) Absorption Spectra of Gossypol Derivatives in the Ultraviolet and Visible Regions. Differences in the absorption spectrum of gossypol and that of dianilinogossypol (Fig. 51) have been adduced [34] as confirmatory evidence of the deep-seated change which occurs in the gossypol molecule during the formation of the dianilino derivative. The shift of

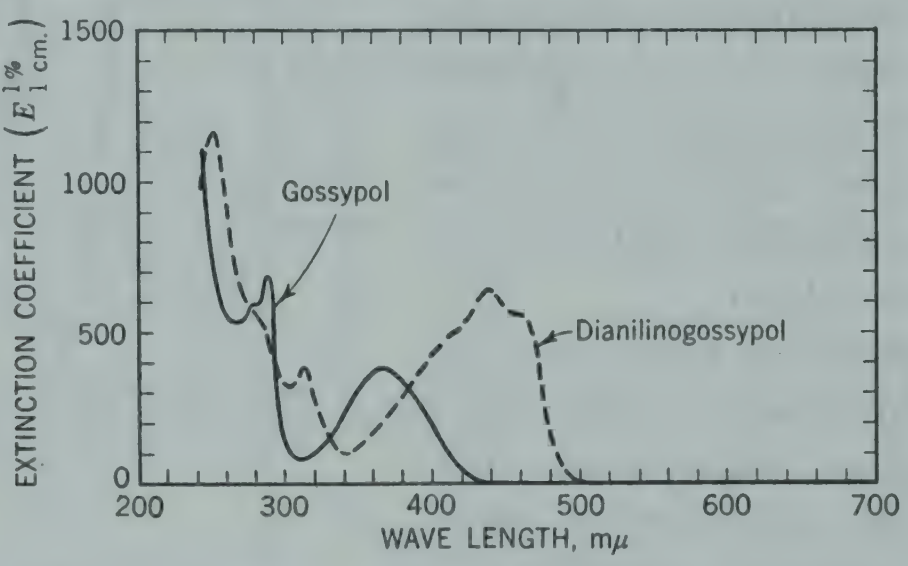


Fig. 51. Absorption spectra of chloroform solutions of gossypol and dianilinogossypol.[34]

the absorption bands in the spectrum of dianilinogossypol indicates the formation of additional conjugated double bonds during the reaction. Considered in conjunction with the chemical reactions of dianilinogossypol and the absorption spectrum of gossypol in polar solvents, the assumption that the reaction of gossypol with aniline involves one or more enolizable carbonyl groups seems entirely tenable.

Adams and Kirkpatrick [65] determined the absorption spectra of a number of gossypol derivatives and compared them with that of gossypol. On the basis of their observations, they were able to make certain deductions concerning the extent to which the structure of gossypol was modified during the formation of the derivatives. For example, since the absorption spectra of gossypol and dimethoxygossypol were very similar, it was con-

[91] A. Smakula, *Angew. Chem.*, **47,** 657–665 (1934).
[92] H. Booker, L. K. Evans, and A. E. Gillan, *J. Chem. Soc.*, **1940,** 1453–1463.

cluded that these compounds were of closely related configuration as had previously been demonstrated by chemical means.

The characteristic absorption at 360 mμ of gossypol and dimethoxygossypol was not observed in the spectra of tetramethoxy-, hexamethoxy-, or hexaacetoxygossypol. Since it had previously been observed that these derivatives exhibit none of the aldehydic reactions characteristic of gossypol, it was concluded that the absorption at 360 mμ is characteristic of the aldehydo-tautomerism of this compound.

Also on the basis of absorption spectra, Adams and Kirkpatrick concluded that hexamethoxygossypol, hexamethoxyapogossypol, and hexamethoxydesapogossypol possessed very similar or identical basic nuclei, and differed only with respect to substituents. However, as may be seen

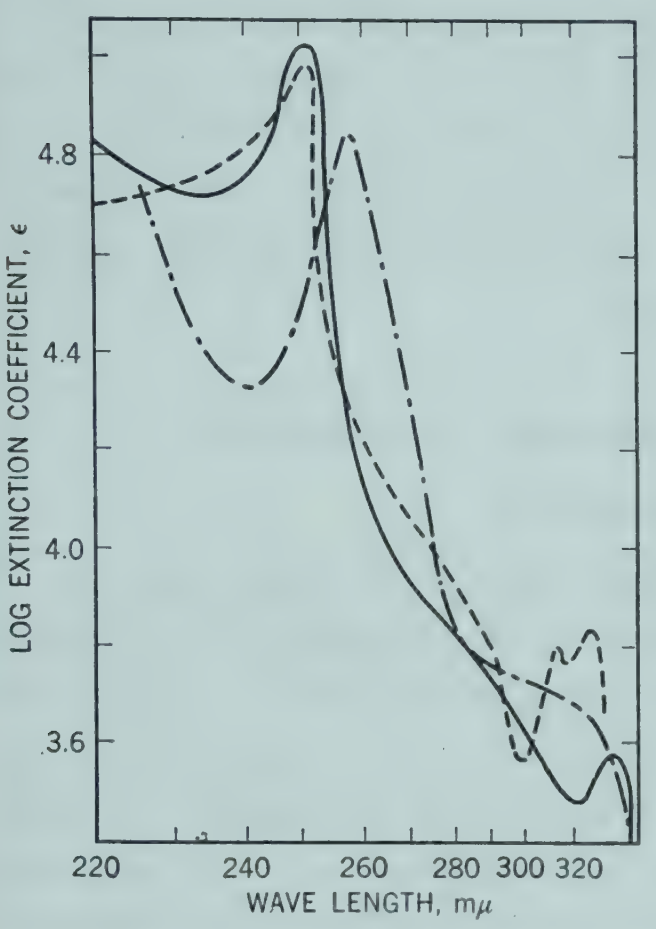


Fig. 52. Absorption spectra of hexamethoxygossypol—, hexamethoxyapogossypol--, and hexamethoxydesapogossypol·—.[65]

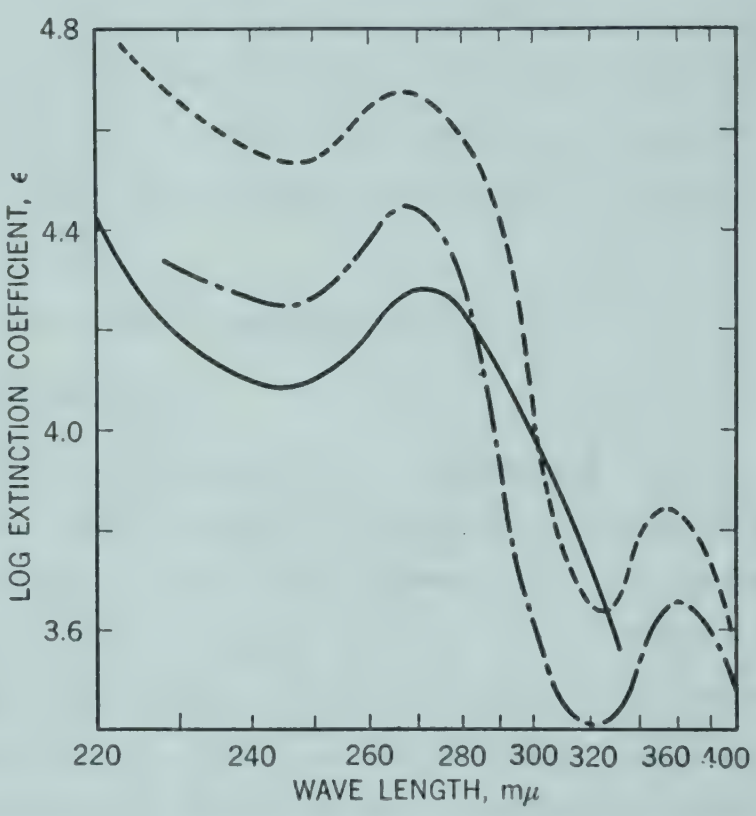


Fig. 53. Absorption spectra of tetramethoxyapogossypolone—, tetramethoxygossypolone--, tetramethoxygossypolonic acid·—.[65]

in Figure 52, the absorption spectra of these compounds do not seem to be sufficiently similar to justify these conclusions.

The products formed upon oxidation of the afore-mentioned ethers exhibit absorption bands of reduced intensity, which are displaced toward longer wave lengths (Fig. 53). Reductive acetylation of the oxidation products causes reversion of the absorption spectra to the pattern characteristic of the ethers. Consequently, it was inferred that the oxidation reactions involve conversion of naphthalene to naphthoquinone derivatives.

The marked difference between the absorption spectrum of anhydrogossypol and that of other gossypol derivatives was attributed to deep-seated changes in the gossypol molecule involving the formation of a new unsaturated ring and alteration of the electronic configuration of the basic ring structure.[65]

(d) Infrared Absorption Spectra of Gossypol and Gossypol Derivatives. Investigation of the infrared absorption spectrum of gossypol in the region from one to ten microns by Zamyschlyaeva and Krivich [93] has been interpreted to indicate the presence in the gossypol molecule of hydrocarbon side chains, and carbonyl and hydroxyl groups. Some evidence for the presence of ethylene linkages was also obtained.

The same investigators [94] determined the infrared absorption spectra of dianilinogossypol, hexaacetoxygossypol, hexaacetoxydianilinogossypol, and gossypol dioxime in the region from 1.5 to 9 microns. Comparison of the spectra of gossypol and the acetyl derivatives indicated that the hydroxyl groups disappeared and the carbonyl groups were possibly changed in these derivatives. In the aniline derivatives the carbon-hydrogen bond was found to be weakened.

B. Cottonseed Pigments Related to Gossypol

1. Gossypurpurin

(a) Isolation. Although the pigment glands of many samples of cottonseed are dark purple in color, and aqueous extracts of cottonseed meal are frequently observed to contain purple material in suspension, isolation of a purple pigment from cottonseed was accomplished only recently.[29] This naturally occurring, purple-colored, cottonseed pigment, named gossypurpurin, from gossy(pium)purpurin, was first obtained from the mixed crystals which it forms with gossypol. These mixed crystals occur as a red material which separates from chloroform extracts of cottonseed. The red crystalline product had previously been assumed to be homogeneous [43] and had therefore been named "red gossypol." Further investigation [29] of "red gossypol" demonstrated that it was a mixture of gossypol containing very small amounts of gossypurpurin.

Gossypurpurin was first separated from gossypol by adsorption on a column of tricalcium phosphate from a toluene solution of "red gossypol." Since gossypurpurin is very strongly adsorbed, whereas gossypol is not, it developed as a purple zone at the top of the column after exhaustive washing of the adsorbent with toluene. The gossypurpurin can subse-

[93] A. M. Zamyschlyaeva and S. S. Krivich, *J. Gen. Chem. U.S.S.R.*, **7**, 1969–1971 (1937); *Chem. Abst.*, **32**, 559 (1938).

[94] A. M. Zamyschlyaeva and S. S. Krivich, *J. Gen. Chem. U.S.S.R.*, **8**, 319–329 (1938); *Chem. Abst.*, **32**, 5303 (1938).

quently be eluted only with polar solvents in which it is very unstable, so that adsorption does not constitute a satisfactory method for its isolation.

Gossypurpurin was also isolated from "red gossypol" by repeated recrystallization of the mixed crystals from mixtures of chloroform and petroleum naphtha, followed by extraction of residual gossypol with ethyl acetate at room temperature. It was observed, as shown in Figure 54, that as the color of the recrystallized product deepened from red to purple the relative heights of the absorption maxima at 530 and 570 mμ increased; whereas the height of the absorption band at 365 mμ decreased. Since the intensities of the absorption bands at 530 and 570 mμ appear to maintain a constant relation to each other, it may be assumed that these bands are characteristic of the purple pigment, and can serve as a guide for isolating and purifying gossypurpurin.

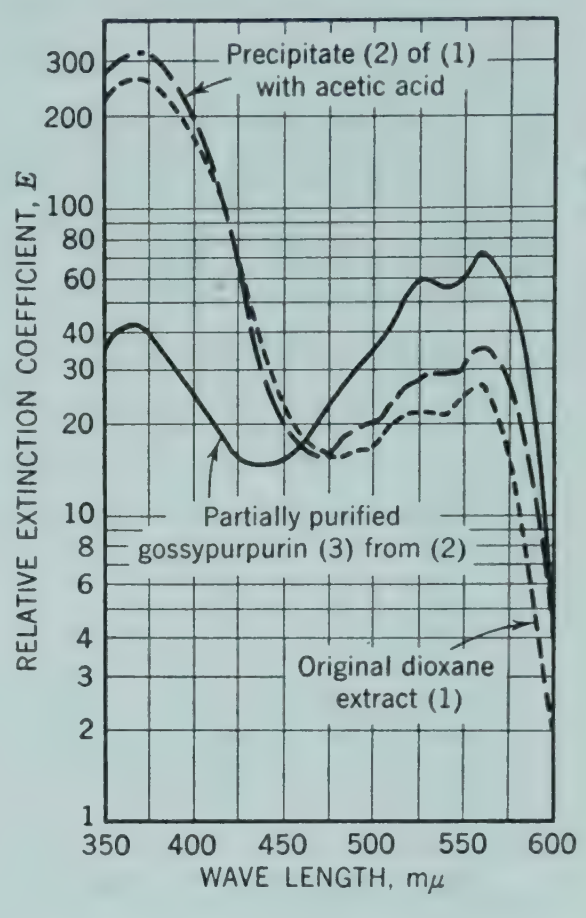


Fig. 54. Progressive changes in absorption spectrum with purification of gossypurpurin.[29]

(b) Preparation and Purification. Because of the very low concentration in which gossypurpurin occurs in cottonseed,[39, 95] it is not readily obtained from this source. Gossypol constitutes the best source of gossypurpurin, since the former is the principal pigment of cottonseed and can be converted to gossypurpurin.

However, it appears that all of the factors affecting the formation and subsequent stability of gossypurpurin have not been determined; so that both small and variable yields of gossypurpurin are obtained by the only method yet devised[95] for its preparation.

Since preliminary purification of gossypol does not appear to be necessary for its conversion to gossypurpurin, ethereal extracts of cottonseed are treated directly for the preparation of this compound.

An ethyl ether extract of cottonseed is in turn extracted with dilute aqueous ammonium hydroxide containing sodium dithionite. Upon allowing the alkaline extract to stand for about an hour, an amber-colored solid separates. Aqueous hydrochloric acid is added to the alkaline suspension until the *p*H has been reduced to 8.4, and the mixture is then extracted with ethyl ether. Glacial acetic acid is added to the ethereal extract and the mixture is heated on a steam bath until all of the ether has evaporated. The purple precipitate thus obtained is washed with

[95] C. H. Boatner, C. M. Hall, R. T. O'Connor, L. E. Castillon, and M. C. Curet, *J. Am. Oil Chem. Soc.*, **24**, 97–106 (1947).

petroleum naphtha (Skellysolve F). In order to remove acetic acid from the mixture of gossypurpurin and gossypol-acetic acid, the latter is heated in aqueous suspension on a steam bath for several hours.

Gossypurpurin is freed of admixed (nonreacted) gossypol by repeated extraction with 95% ethanol, in which gossypol is very soluble and gossypurpurin only slightly soluble. Because of the slight solubility of gossypurpurin in most organic solvents and its extreme instability in the few solvents in which it is soluble, no method for its further purification has yet been devised. It has not been obtained in sufficiently large crystals to permit determination of its crystalline form, nor has its purity been established.

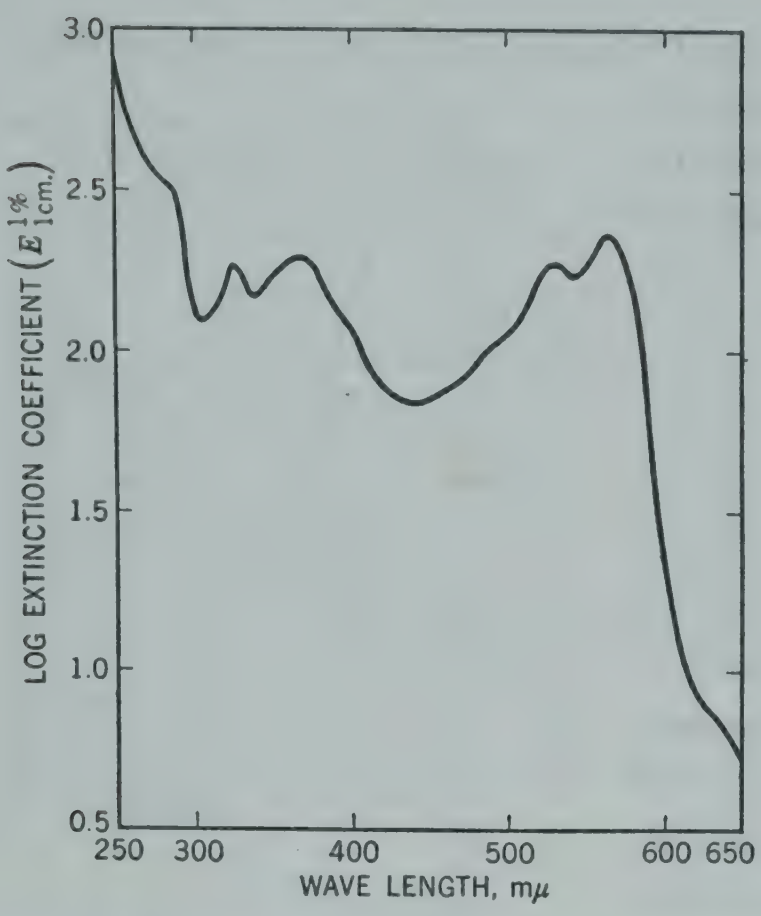


Fig. 55. Absorption spectrum of a chloroform solution of gossypurpurin.[95]

(c) Properties. Gossypurpurin is a dark purple microcrystalline solid which appears almost black. It melts at 200–204° C., and contains carbon, 63.15%; hydrogen, 6.15%; nitrogen, 3.09%; and ash, 2.86%.

Chloroform solutions of gossypurpurin prepared and purified according to the procedure described above are purple-colored, and exhibit the absorption spectrum shown in Figure 55. Its spectrum comprises two absorption bands in the ultraviolet wave length region having maxima at 326 to 327 mμ, $E^{1\%}_{1cm.} = 184.6$, and at 370 to 371 mμ, $E^{1\%}_{1cm.} = 195.7$, and two absorption bands in the visible wave length region with maxima at 530 mμ, $E^{1\%}_{1cm.} = 186.7$, and at 565 to 566 mμ, $E^{1\%}_{1cm.} = 225.7$.

Gossypurpurin is very soluble in dioxane, acetone, and pyridine; slightly soluble in chloroform, ethyl acetate, diethyl ether, and benzene; very slightly soluble in petroleum naphtha, methanol, and ethanol; and insoluble in cottonseed oil, water, and concentrated sulfuric acid.

In the solid state gossypurpurin appears to be relatively stable, but in solution it decomposes under a variety of conditions with the formation of a pale yellow pigment which differs from gossypol. The stability of dissolved gossypurpurin depends to a very large extent upon the solvent employed, which is analogous to the behavior reported by Podol'skaia [43] for "red gossypol." Gossypurpurin exhibits decreasing stability in solution according to the following order of the solvents: chloroform, ethyl

acetate, diethyl ether, dioxane, methanol, ethanol, and pyridine. In methanol, ethanol, acetone, or pyridine solutions, gossypurpurin is completely converted to its yellow decomposition product within a few minutes.

Solutions of gossypurpurin are rapidly decomposed in the presence of traces of acid or base. They are also unstable to light and heat. The following reagents do not appear to affect the rate of decomposition when they are added to solutions of gossypurpurin: hydroquinone, ascorbic acid, sodium dithionite, hydrogen peroxide, and calcium carbonate. On the other hand, addition of sodium citrate or diphenylamine accelerates the formation of the yellow decomposition product.[29] In the absence of any trace of acid or base, and when protected from light and maintained at a temperature of 3.3° C., chloroform extracts of cottonseed have been preserved without decomposition of gossypurpurin for periods as long as seventy-two hours.[95] Chloroform solutions of gossypurpurin are effectively protected from the action of diffused light if prepared and stored in low-actinic glassware.

Gossypurpurin forms an unstable blue reaction product with chloroform solutions of antimony trichloride, which exhibits a characteristic absorption spectrum with a single maximum at 650 mμ. The reaction product with ferric chloride is purple. Bromine is readily absorbed by solutions of gossypurpurin in ethanol.

The purple suspension frequently observed in aqueous extracts of cottonseed has been identified [29] as a combination of protein with gossypol and gossypurpurin. Both of the pigments can be completely removed from the protein by extraction with dioxane. The ease with which the pigments can be separated from the pigment–protein complex, coupled with the ready adsorption of gossypurpurin on a weak adsorbent such as tricalcium phosphate, suggests that the chromoprotein is formed by adsorption.

(d) Structure. In view of the absence of any convincing evidence as to the purity of the best preparation of gossypurpurin yet reported, or any experimental data indicating its molecular weight, conclusions concerning its probable structure and relation to gossypol are necessarily provisional.

The high content of nitrogen and the formation of gossypurpurin by preliminary treatment of gossypol with ammonium hydroxide suggests that nitrogen constitutes an intrinsic part of the gossypurpurin molecule. On the other hand, if the transitory purple colors noted by Marchlewski,[7] Carruth,[8] and Clark [9] upon reaction of strong bases with gossypol are due to the formation of gossypurpurin, it must be concluded that the pigment is a nitrogen-free, oxidative degradation product of gossypol. However, the observation during the cooking of cottonseed that the formation of gossypurpurin is not accelerated when the seed is finely

ground makes it appear improbable that gossypurpurin is formed as the result of the oxidation of gossypol. Moreover, although the purple colors formed in alkaline solutions of gossypol are too unstable to permit identification of their absorption spectra, many of the purple products formed during treatment of cottonseed extracts have been examined spectrophotometrically and found to differ from gossypurpurin.

Since the most highly purified preparation of gossypurpurin which has been reported [95] was not recrystallized during purification, it is possible that its high ash content can be attributed to inorganic impurities entrained from the extract during its precipitation. The carbon and hydrogen values for gossypurpurin, recalculated on an ash-free basis, differ very little from those obtained for gossypol. Consequently, unless the molecular weights of the two pigments are very dissimilar, it does not appear probable on this basis that gossypol undergoes extensive oxidation during its conversion to gossypurpurin.

The purple color produced by reaction with ferric chloride is indicative of a hydroxyl group in a position adjacent to a carboxyl group. The location of absorption bands of gossypurpurin in the long wave length region indicates that the molecule possesses a complex structure and probably contains a large number of conjugated double bonds. The probability that gossypurpurin possesses a more complex structure than gossypol is further indicated by its greater tendency toward adsorption on protein and other adsorbing materials such as tricalcium phosphate.

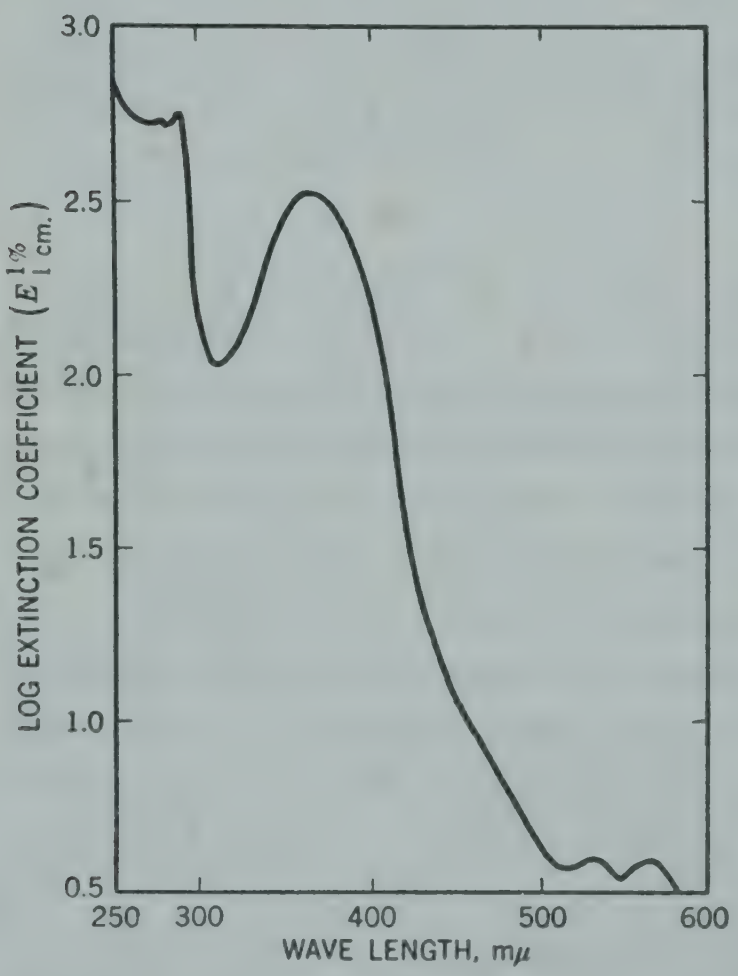


Fig. 56. Absorption spectrum of a chloroform solution of "red gossypol."

(e) "Red Gossypol." Podol'skaia's observation,[43] of the similarity in the absorption spectra and stabilities of freshly prepared chloroform extracts of cottonseed and the red crystals obtained from the precipitate resulting from the evaporation of such extracts, led her to the conclusion that "red gossypol" constitutes the naturally occurring form of gossypol in cottonseed. She observed that chloroform extracts of cottonseed as well as chloroform solutions of "red gossypol" changed on standing from red to yellow. At the same time the absorption bands at 535 and 570 mμ disappeared, while those at 365 mμ,

characteristic of gossypol solutions, remained unaltered. She concluded that "red gossypol" was converted to gossypol.

"Red gossypol" was also prepared by Campbell, Morris, and Adams,[25] who confirmed Podol'skaia's observations concerning its instability. The absorption spectrum [96] of the "red gossypol" prepared by the American investigators (shown in Fig. 56) indicated the presence of a very small amount of gossypurpurin. Application of the antimony trichloride spectrophotometric method for the determination of gossypol [46] demonstrated a content of 68.3% gossypol.

It is probable that Podol'skaia's "red gossypol" contained similar proportions of gossypol and gossypurpurin, and, consequently, her observations concerning the similarity of the properties of "red gossypol" and gossypol might have been due to the preponderance of gossypol in her preparations.

The relative instability of "red gossypol" in various organic solvents reported by Podol'skaia may be attributed to the presence of gossypurpurin in the mixture. It also appears probable that the difference in properties of crystalline "red gossypol" and gossypol which were described by the same author can be attributed to gossypurpurin. Crystalline "red gossypol" exhibits strong pleochroism and direct extinction in contrast to the birefringence and parallel extinction exhibited by crystalline gossypol.

2. Gossycaerulin

In the first recorded investigation of the pigments of cottonseed, Kuhlmann [97] reported the formation of a brilliant blue coloring matter when acidified cottonseed oil foots were subjected to steam distillation for the recovery of fatty acids. It was observed that, when the foots were heated at 100° C. for four to five hours with 3 to 4% sulfuric acid, a dark blue mass was formed. The product was washed with water, and then recrystallized from a mixture of ethanol and petroleum naphtha. Kuhlmann reported a number of the properties of this blue compound, but discontinued his investigation upon determining that its instability to light prevented its utilization as a dye.

Interest in the blue pigment of cottonseed was recently stimulated by the observation [33, 95] that, although it does not appear to be a constituent of raw cottonseed, it is formed in varying amounts during cooking of cottonseed, and that the amount which is formed during cooking increases as the gossypol concentration decreases. It was further observed that the condition of the seed, particularly its content of moisture and its *p*H, and length of cooking influenced the extent to which gossypol is converted

[96] Sample furnished by R. Adams.
[97] F. Kuhlmann, *Compt. rend.*, **53,** 444–452 (1861).

into the blue pigment. The pigment has been named gossycaerulin, from gossy(pium)caerulin.

(a) Preparation. Since the changes occurring during the cooking of cottonseed made it appear probable that gossycaerulin is a derivative of gossypol, its preparation from this latter pigment was investigated.[33] The amount of gossycaerulin formed under different conditions was estimated on the basis of the blue color of its acidified chloroform solutions and the broad absorption band with a maximum at 610 mμ which they exhibit.

It was found, by heating various acidified solutions of gossypol, that this pigment is converted to gossycaerulin only in alcohol solutions or aqueous suspensions. Comparison of different alcohols and acids showed that methanol is the best medium and sulfuric acid the most effective acid for this preparation.

The reaction of gossypol in acidified alcoholic solution under the influence of heat was found to follow two alternative paths. When the reaction is carried out at low temperatures or in the presence of dilute sulfuric acid, preponderant amounts of a pale yellow compound are formed. This latter compound may be detected by means of the absorption spectrum of its antimony trichloride reaction product, which exhibits an absorption band with a maximum at 430 mμ. This absorption spectrum differentiates it sharply from the antimony trichloride reaction product of gossypol which has absorption maxima at 520 and 380 mμ and a minimum at 430 mμ,[46] and from that of gossycaerulin which has an absorption maximum at 605 mμ.

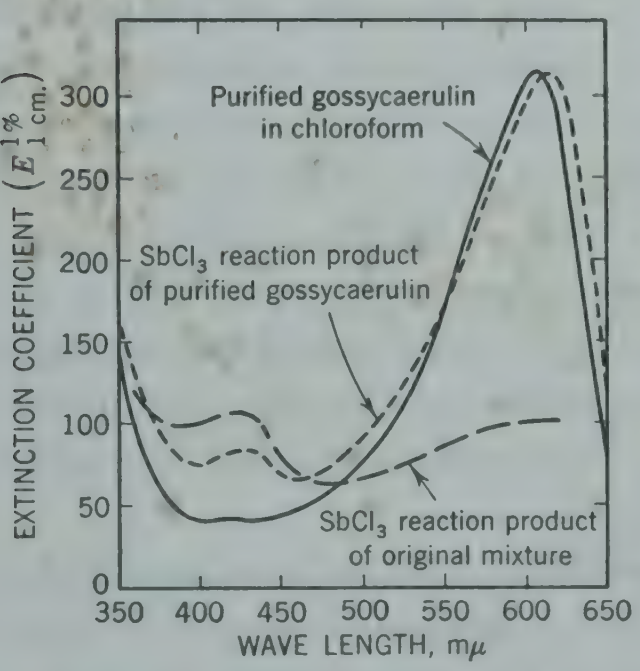


Fig. 57. Absorption spectra of gossycaerulin, and of the antimony trichloride reaction products of gossycaerulin and its by-product.[33]

With higher concentrations of sulfuric acid or upon more prolonged heating, the yield of gossycaerulin is reduced by the formation of a purple reaction product which exhibits a low but broad absorption band with a maximum at 570 mμ, $E^{1\%}_{1cm.} = 98.7$. Apparently, neither the yellow nor the purple reaction product derived from gossypol can be converted into gossycaerulin. No reaction conditions resulting in the formation of gossycaerulin, free of both the yellow and the purple gossypol conversion products, have been found. Since it was found that gossycaerulin can be freed more easily from the yellow than from the purple compound by fractional crystallization, reaction conditions were established to produce the maximum amount of gossycaerulin with the minimum amount of the purple compound.

The best yield of gossycaerulin which has been reported [33] was obtained by heating a 0.2% solution of gossypol in a 3.2% (by volume) solution of sulfuric acid in methanol under reflux on a steam bath for seventy-two hours. The absorption spectrum of the antimony trichloride reaction product of the crude material produced in this manner is reproduced in the lower curve of Figure 57. Evidence of the presence of the yellow by-product can be seen in this absorption spectrum. When the crude product was repeatedly recrystallized from a mixture of diethyl ether and petroleum naphtha (Skellysolve F), a dark blue solid was obtained which melted at 169° C. with decomposition. The solution of this compound in chloroform, acidified with hydrochloric acid, exhibited a well-defined absorption band with maximum at 605 mμ, $E^{1\%}_{1cm.} = 315.4$, and an absorption minimum at 430 mμ, $E^{1\%}_{1cm.} = 40.8$ (Fig. 57). The absorption spectrum of the antimony trichloride reaction product of this blue compound (Fig. 57) in chloroform was similar, except that the absorption maximum was shifted to 610 mμ. However, the value of the specific extinction coefficient at the maximum was exactly the same, namely, 315.4. The secondary absorption maximum at 430 mμ, $E^{1\%}_{1cm.} = 85.7$, exhibited by the antimony trichloride reaction product indicates that not all of the yellow by-product had been removed. On the other hand, the sharpness with which the absorption decreased on the short wave length side of the gossycaerulin absorption band demonstrates the absence of both unreacted gossypol and the purple gossycaerulin–sulfuric acid reaction product.

(b) Properties. Kuhlmann [97] reported that gossycaerulin could be sublimed or distilled *in vacuo,* and the sublimate or distillate thus obtained was described as being slightly soluble in ether, ethanol, chloroform, and carbon disulfide. He obtained microcrystals of gossycaerulin upon recrystallization from a mixture of ethanol and petroleum naphtha. Kuhlmann reported the product to contain 70.24% carbon and 8.35% hydrogen. These values agree closely with those calculated for $C_{30}H_{30}O_8$, the molecular formula proposed for gossypol.[98]

The following derivatives of gossycaerulin were reported by the same investigator. Gossycaerulin reacts with concentrated nitric acid to form a yellow acidic compound which is soluble in alkali, and is reprecipitated in its original form upon addition of acid. It forms insoluble silver and lead salts. Although Kuhlmann reported that the reaction product of gossycaerulin and nitric acid was a mononitrated derivative, he determined only its carbon and hydrogen contents which were reported to be 60.28 and 6.76%, respectively. Kuhlmann also reported that gossycaerulin reacts with chlorine, bromine, and iodine to form well-defined, yellow reaction

[98] Kuhlmann considered the carbon and hydrogen content to agree with the values calculated for $C_{34}H_{24}O_8$.

products. The reported chlorine content, 11.47%, of the chloro derivative indicates it to be a dichloro compound.[99] In the absence of information relative to the nitrogen content of Kuhlmann's compound, and especially in the light of the susceptibility of gossycaerulin to oxidation, speculation concerning its probable formula is not presently justified.[100]

More recently, gossycaerulin has been reported [33] to undergo a reversible color change from blue in acid solution to pale yellow in neutral or alkaline solution. The blue acidic form of the pigment is soluble in methanol, ethanol, isopropanol, amyl alcohol, acetic acid, acetic anhydride, and ether. It is slightly soluble in chloroform; and very slightly soluble in petroleum naphtha (Skellysolve F), benzene, toluene, water, hot saturated aqueous sodium bisulfite, and aqueous sodium hydroxide. The yellow neutral form is soluble in petroleum naphtha (Skellysolve F), toluene, and benzene; slightly soluble in chloroform; and very slightly soluble in methanol, ethanol, and ether. The maximum blue color, measured spectrophotometrically, is exhibited in solutions containing very low concentrations of acid, and appears to be independent of the strength or nature of the acid employed.

Kuhlmann [97] observed the formation of a purple solution upon dissolving gossycaerulin in sulfuric acid. Upon reinvestigation of this reaction it was found,[33] in contrast to Kuhlmann's report, that gossycaerulin is not recovered unchanged when the solution is poured into water. Because of its finely divided condition, the precipitate appears to be blue, but its solution in chloroform is purple and exhibits the absorption band with a maximum at 570 mμ which is characteristic of the gossycaerulin–sulfuric acid reaction product. The color exhibited by solutions of gossycaerulin in concentrated sulfuric acid is in marked contrast to that of gossypol, which forms a brilliant red solution in concentrated sulfuric acid,[8] and is recovered unchanged when the solution is poured into water.[25]

Gossycaerulin forms a purple, thermally stable reaction product with boroacetic acid in acetic anhydride solution, and a blue-purple reaction product with stannic chloride in benzene solution. It is unaffected by hydrogen peroxide at room temperature, but is decomposed to a stable yellow-brown compound by reaction with hydrogen peroxide at elevated temperatures. Reaction at room temperature with lead tetraacetate in benzene or chloroform solution or with ferric chloride in ethanol solution causes gossycaerulin to change from blue to yellow to brown. A similar series of color changes is observed upon its reaction with periodic acid at 3.3° C. Corresponding treatment of gossypol solutions with the foregoing

[99] Calculated for $C_{30}H_{28}O_8Cl_2$; Cl, 11.92%.

[100] Kuhlmann reported the formula of the nitrated derivative as $C_{31}H_{23}O_8(NO_4)$. The calculated carbon and hydrogen content of both mono- and dinitrogossycaerulin differ significantly from the experimentally determined values reported by Kuhlmann.

oxidizing reagents causes a sequence of color changes from yellow to green to yellow to brown.

(c) Structure. Some insight into the structure of gossycaerulin can be obtained from a consideration of its properties and their relation to those of gossypol. The observation that a transient green color is formed during the reaction of gossypol with oxidizing agents which also oxidize gossycaerulin suggests that the latter pigment is an unstable oxidation product of gossypol. The fact that gossycaerulin is permanently altered by solution in concentrated sulfuric acid, whereas gossypol is recovered unchanged, indicates that the former pigment is very much more unstable to oxidation than the latter.

The readily reversible reduction of gossycaerulin, coupled with its origin from the polyphenolic gossypol molecule, indicates that gossycaerulin is a quinone. The purple-colored reaction products observed with boroacetic acid and stannic chloride are characteristic of compounds containing hydroxyl and carbonyl groups in adjacent positions.[76, 77] In view of the ease and reversibility of the reduction of gossycaerulin, it appears probable that the carbonyl groups are quinonoid in nature.

Likewise, the ease and reversibility of the color change which solutions of gossycaerulin undergo upon successive treatment with acid and base are indicative of tautomerism involving ionization. On the basis of their colors, relative solubilities, and mode of formation, it appears probable that the yellow form of gossycaerulin is a neutral molecule, whereas the blue form is a substituted carbonium ion.

These conclusions concerning the formation of a blue carbonium ion cannot be reconciled with Kuhlmann's observation that the blue form produces no ash. However, with the development of methods for the preparation of gossycaerulin in amounts adequate for elementary analysis, it should be possible to test the validity of these conclusions by the preparation and analysis of different salts.

(d) Gossycaerulin–Sulfuric Acid Reaction Product. Heating of methanol solutions of gossypol containing more than 10% (by volume) of sulfuric acid for periods of twenty-four hours, or heating of solutions containing less sulfuric acid for more prolonged periods, results in the formation of a purple reaction product of gossycaerulin with sulfuric acid. This product is also formed by heating methanol solutions of gossycaerulin with concentrated sulfuric acid, and under these conditions the rate of its formation is proportional to the concentration of sulfuric acid. The product also forms immediately upon dissolving gossycaerulin in concentrated sulfuric acid.

Acidified chloroform solutions of the purple compound exhibit a broad absorption band with a maximum at 570 mμ, $E^{1\%}_{1cm.} = 98.7$, a minimum

at 440 mμ, $E^{1\%}_{1cm.} = 39.0$, and a slowly increasing absorption toward the near ultraviolet wave length region. Reaction with antimony trichloride shifts the absorption maximum to 580 mμ, $E^{1\%}_{1cm.} = 112$, and the minimum to 470 mμ, $E^{1\%}_{1cm.} = 63.8$. Treatment of a methanol solution of the purple compound with ammonia changes the solution to blue-green, with no absorption band appearing in the visible wave length region. Upon acidification of the solution, the original purple color is restored.

Treatment of ethanol solutions of the purple compound with sodium dithionite or bisulfite causes the color to fade to yellow, but the original color is restored upon treatment of the solution with hydrogen peroxide or shaking it in air. Reaction of chloroform solutions of the purple compound with lead tetraacetate results in the formation of a yellow solution which cannot be restored to the original purple color by treatment with reducing agents. No methods for reconversion of the purple reaction product to gossypol or gossycaerulin have been reported.

It may be concluded, on the basis of the ready and reversible reduction of the purple compound, coupled with its mode of formation from gossypol and gossycaerulin, that the gossycaerulin–sulfuric acid reaction product is probably a quinone and an unstable oxidation product of gossycaerulin. The reversible color changes produced by successive treatments with acid and base suggest that it is capable of existing in two tautomeric modifications resulting from rearrangements similar to those occurring in the gossycaerulin molecule under similar conditions.

3. Gossyfulvin

The orange-colored pigment, gossyfulvin, recently isolated from an ethereal extract of cottonseed [32] is of considerable theoretical and technical interest. It has been reported that gossyfulvin can be converted directly to gossypol by treatment with acid,[32] and that it is structurally identical with dianilinogossypol, a relatively simple gossypol derivative.[34] It appears only rarely in cottonseed and has so far been detected only in seed which has been stored at a high moisture content. Gossyfulvin has also been detected in several samples of hydraulic-pressed cottonseed oil and meal, and in several samples of cottonseed oil extracted with petroleum naphtha.

(a) Preparation.[32] Gossyfulvin has been prepared from an ethereal extract of cottonseed from which it was obtained after the separation of gossypol, oil, fatty acids, and other materials present in the original extract. The procedure followed for its separation is shown in Figure 58. An ethereal extract of cottonseed was in turn extracted with a dilute aqueous solution of sodium hydroxide containing sodium dithionite. The yellow-colored ethereal layer which separated from the aqueous extract when the

*p*H of the latter was reduced to 7 to 7.5 contained gossypol and the orange pigments. Gossypol precipitated completely as gossypol-acetic acid within a short time after the addition of acetic acid to the ethereal solution. The orange pigments remaining in solution precipitated very slowly over a period of several weeks.

This precipitate, which comprises a mixture of two or more pigments, is readily fractionated by extraction with hot acetone. The insoluble resi-

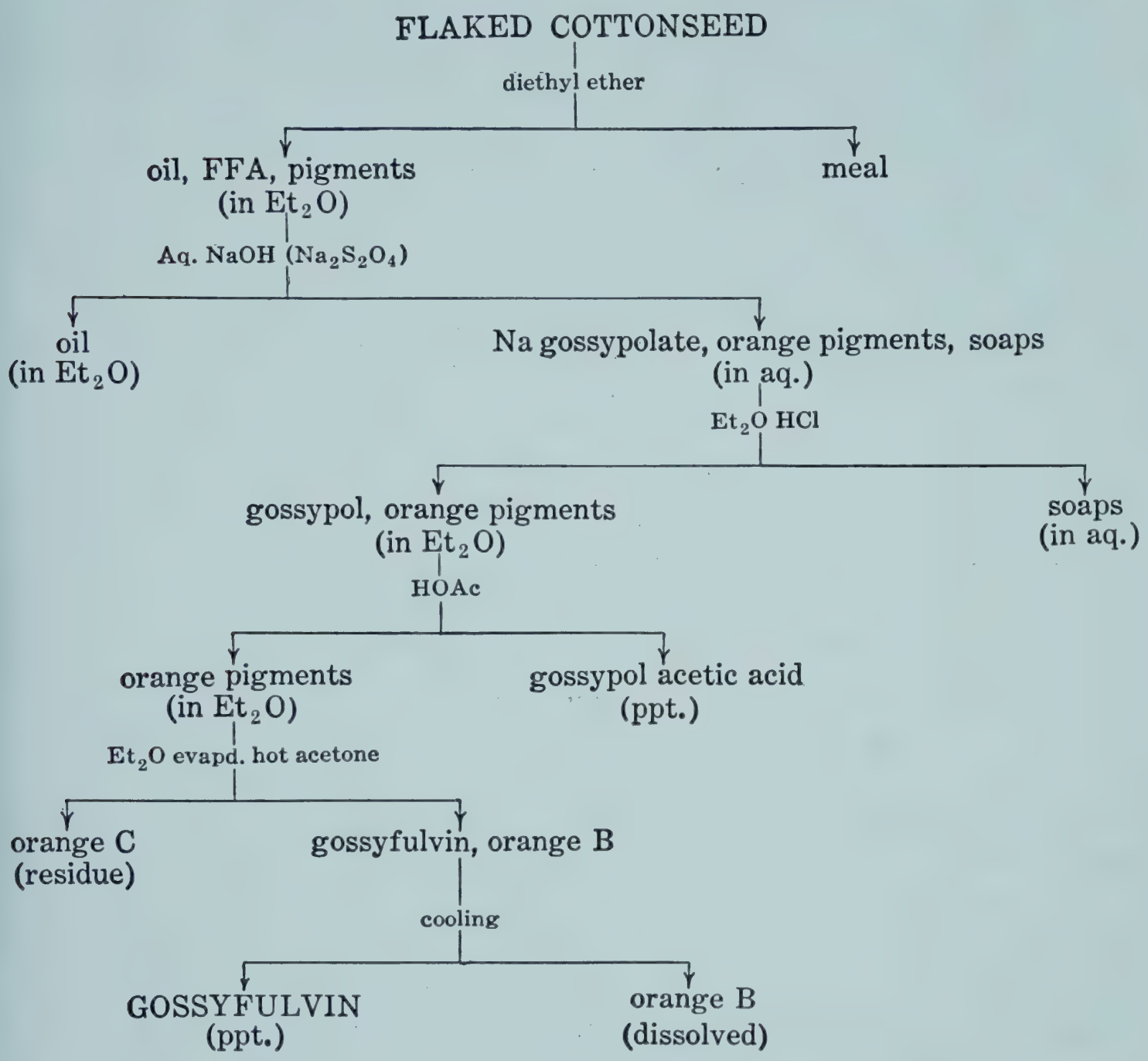


Fig. 58. Procedure for isolation of gossyfulvin.

due is a pale orange-colored pigment. Glistening bronze-colored needles crystallize from the acetone solution upon cooling, leaving a dark reddish-orange pigment in solution. Of the various orange-colored pigments contained in the original precipitate, only gossyfulvin obtained from the fraction soluble in hot, and insoluble in cold acetone has been investigated.

(b) Properties.[32] Pure gossyfulvin prepared by three successive recrystallizations of crude gossyfulvin from mixtures of chloroform and diethyl ether at 3.3° C. forms rather large, orange-colored rhombs (Fig. 59), changing at 212° C. to a more deeply colored form which melts with de-

composition at 238–239° C. It is very soluble in 2,4-dioxane; moderately soluble in chloroform, aniline, carbon disulfide, and hot acetone; very slightly soluble in ethanol, cold acetone, and diethyl ether; and insoluble in aqueous sodium hydroxide and saturated aqueous sodium bisulfite.

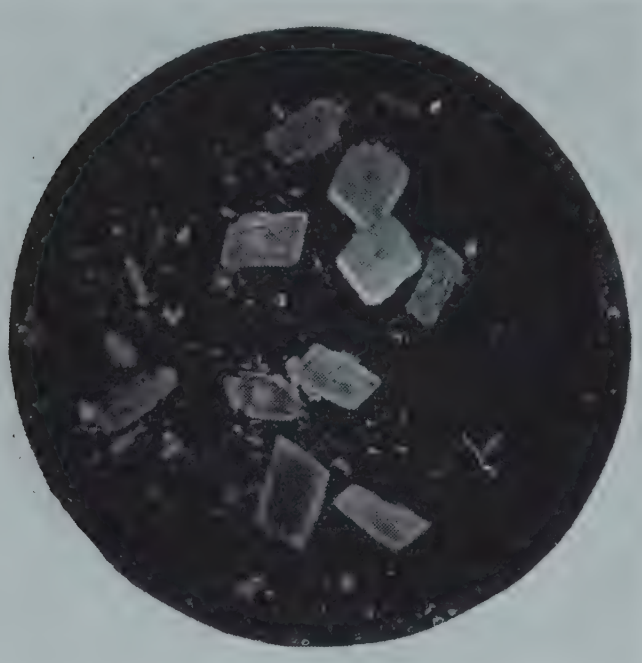


Fig. 59. Photomicrograph (×31) of crystalline gossyfulvin between crossed Nicols.[34] (By M. E. Jefferson and F. B. Kreeger.)

Gossyfulvin was reported to have the following elementary composition: carbon, 68.90%; hydrogen, 5.62%; nitrogen, 4.61%; calculated for $C_{34}H_{34}N_2O_8$: carbon, 68.23%; hydrogen, 5.69%; nitrogen, 4.68%.

As shown in Figure 60, gossyfulvin in chloroform solution exhibits a broad absorption band in the visible wave length region, having the principal maximum of 439–440 mμ, $E^{1\%}_{1\text{cm.}} = 649.4$, and two bands in the ultraviolet having maxima at 312–313 mμ, $E^{1\%}_{1\text{cm.}} = 370.9$, and at 261–262 m$\mu$, $E^{1\%}_{1\text{cm.}} = 1215.6$. In contrast to the stable red reaction product formed by gossypol with antimony trichloride,[46] gossyfulvin forms an unstable yellow product with a single absorption band in the visible wave length region having a maximum at 460 mμ, $E^{1\%}_{1\text{cm.}} = 522$.

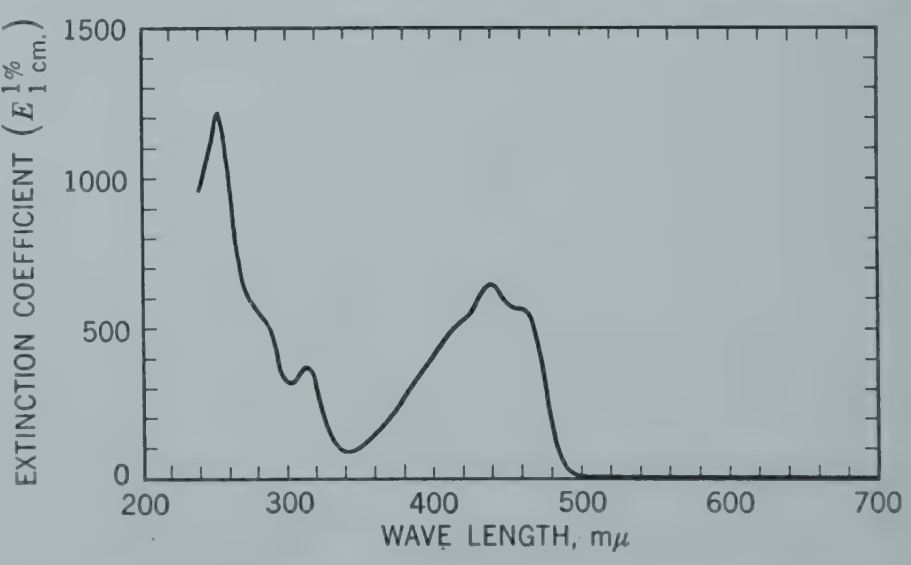


Fig. 60. Absorption spectrum of gossyfulvin in chloroform.[34]

Gossyfulvin differs from gossypol in its failure to react with aniline, Fehling's solution, or fuchsin–aldehyde reagent, and by its insolubility in alkali. With the appropriate reagents it forms a dioxime and a di(2,4-dinitro)phenylhydrazone having carbon, hydrogen, and nitrogen contents identical with the corresponding derivatives of gossypol. However, the melting points of the oxime and dinitrophenylhydrazones formed by gossyfulvin, 204.5° C. and 230–230.5° C., respectively, differ from those of the corresponding gossypol derivatives. Mixtures of the corresponding derivatives formed by gossypol and gossyfulvin melt over a wide range of temperature, thus indicating that they are different compounds.

Acetylation of gossyfulvin with acetic anhydride in the presence of either sodium acetate or pyridine yields a brilliant yellow solid. After recrystallization from ether and petroleum naphtha (Skellysolve F) the yellow product melts sharply at 185–185.25° C. The acetyl content of acetylated gossyfulvin is 34.6%, which agrees with the value calculated for hexaacetoxygossypol.

When choloroform solutions of gossyfulvin are shaken with a few drops of concentrated aqueous solutions of hydrochloric, sulfuric, phosphoric, or trichloroacetic acid, gossypol is formed in yields of 82 to 86%, based on the weight of gossyfulvin treated. Chloroform solutions of gossyfulvin are not affected by treatment with dry hydrogen chloride, or glacial or dilute acetic acid.

(c) Structure and Relationship to Gossypol. The ready conversion of gossyfulvin to gossypol indicates a direct relationship between these two pigments. The values of the corresponding specific extinction coefficients at critical wave lengths of chloroform solutions of gossyfulvin and dianilinogossypol (Table 66) are identical, within the limits of experi-

TABLE 66

Specific Extinction Coefficients ($E^{1\%}_{1cm.}$) of Gossyfulvin and Dianilinogossypol in Chloroform at Points of Characteristic Absorption

Wave length, mμ	Description	Specific extinction coefficient	
		Gossyfulvin	Dianilinogossypol
251–252	Maximum	1215.6	1168.6
302–303	Minimum	311.7	314.4
312–313	Maximum	370.9	372.8
341	Minimum	87.79	94.0
439–440	Maximum	649.4	—
437–439	Maximum	—	634.4
456–462	Shoulder	571.5	555.3–555.9

mental error, throughout the ultraviolet and visible wave length regions. Consequently, it may be concluded that the basic structure of gossyfulvin is the same as that of dianilinogossypol.

Dianilinogossypol is one of the most stable derivatives of gossypol. It is formed by the reaction of one molecule of gossypol with two molecules of aniline with the loss of two molecules of water.[9] The tautomeric structures which have been proposed for dianilinogossypol [72] closely resemble those proposed for gossypol and differ only in the substitution of two anilino groups for the two doubly bound oxygen atoms of the carbonyl groups of gossypol. Since the absorption spectrum and, therefore, the basic structure of gossyfulvin is identical with that of dianilinogossypol, but

different from that of gossypol, it appears that the reactions occurring during the formation of either of these compounds from gossypol involve a greater change than that which would result from the simple substitution of nitrogen-containing groups for the oxygen atoms of the carbonyl groups of gossypol.

Since the specific extinction coefficients of gossyfulvin and dianilinogossypol are identical, it must be supposed that either their molecular weights are the same, or the two phenyl groups in dianilinogossypol produce an *enhancement* of its absorption. Gossypol is obtained by acid hydrolysis of gossyfulvin in amounts equal to as much as 86.6% of the weight of gossyfulvin treated; whereas the gossypol molecule represents only 77.6% of the weight of dianilinogossypol. On the assumption that gossyfulvin is a simple monomolecular rather than polymolecular gossypol derivative, its maximum molecular weight can be calculated to be 598 compared to 668 for dianilinogossypol. Consequently, it may be assumed that the presence of two phenyl groups in dianilinogossypol produces an enhancement of its absorption over that of gossyfulvin.

The elementary composition of gossyfulvin differs significantly from that of dianilinogossypol, but it is very similar to that reported for diaminogossypol (Table 67). Moreover, Adams and co-workers [72] postu-

TABLE 67

Comparison of Gossyfulvin with Gossypol and Its Simple Nitrogen Derivatives

Compound	M.p., °C.	Formula	Elementary composition, %					
			Calculated			Found		
			C	H	N	C	H	N
Gossypol	181–181.5	$C_{30}H_{30}O_8$	69.50	5.79	—	68.46	5.88	—
Diaminogossypol[a]	228–230	$C_{30}H_{32}N_2O_6$	69.76	6.20	5.42	69.56	6.53	5.17
Dianilinogossypol	302–303	$C_{42}H_{40}N_2O_6$	75.45	5.99	4.19	75.34	6.13	4.18
Gossyfulvin	238–239	$C_{34}H_{34}N_2O_8$	68.23	5.69	4.68	68.90	5.62	4.61

[a] Values reported by R. F. Miller and R. Adams, *J. Am. Chem. Soc.*, **59**, 1736–1738 (1937).

lated that these gossypol derivatives are of identical structure. Consequently, it might appear that gossyfulvin represents merely impure diaminogossypol. However, as may be seen in Table 67, the melting point of gossyfulvin is higher than that reported for diaminogossypol. Gossyfulvin and diaminogossypol also differ with respect to solubility and stability. Diaminogossypol, dissolved in diethyl ether, is reported [49] to decompose with evolution of ammonia and to revert to gossypol. Gossyfulvin is almost completely insoluble in diethyl ether and, although it is

unstable in solvents in which it is soluble, in the absence of strong acids it does not liberate ammonia, but undergoes change without the loss of nitrogen. Diaminogossypol is reported to be hydrolyzed to gossypol by being merely warmed in acetic acid, whereas treatment with strong concentrated acids is required to convert gossyfulvin to gossypol. The formula proposed for gossyfulvin, $C_{34}H_{34}N_2O_8$, does not correspond to that of any simple gossypol derivative.

That the structures, as well as the interrelations, of gossypol, gossyfulvin and dianilinogossypol are very complex was shown [34] by comparison of the composition and properties of their dinitrophenylhydrazones and dioximes (Table 68). Although their melting points are quite dif-

TABLE 68

Composition and Melting Points of Dioximes and Di-dinitrophenylhydrazones Formed by Gossypol, Gossyfulvin, and Dianilinogossypol[a]

Compound	M.p.,°C.	Formula	Elementary composition found, %[b]		
			C	H	N
Dioxime of gossypol	312	$C_{30}H_{32}O_8N_2$	65.70	5.72	5.04
Dioxime formed by gossyfulvin	204.5	$C_{30}H_{32}O_8N_2$	65.35	6.02	5.00
Dioxime formed by dianilinogossypol	221–221.5	$C_{30}H_{32}O_8N_2$	65.25	6.03	5.33
Di-dinitrophenylhydrazone of gossypol	268–269[c]	$C_{42}H_{38}O_{14}N_8$	55.10	3.65	11.50
Di-dinitrophenylhydrazone formed by gossyfulvin	230–230.5[c]	$C_{42}H_{38}O_{14}N_8$	—	—	9.27
Di-dinitrophenylhydrazone formed by dianilinogossypol	145–146[c]	$C_{42}H_{38}O_{14}N_8$	55.99	4.58	11.22

[a] C. H. Boatner, R. T. O'Connor, C. S. Samuels, and M. C. Curet, *J. Am. Chem. Soc.*, **69**, 1268–1271 (1947).

[b] Composition calculated for gossypol dioxime, $C_{30}H_{32}O_8N_2$: C, 65.66; H, 5.84; N, 5.12. Composition calculated for gossypol di-dinitrophenylhydrazone, $C_{42}H_{38}O_{14}N_8$: C, 57.40; H, 4.33; N, 12.75.

[c] Determined with a Fisher micromelting point apparatus.

ferent, the elementary compositions of corresponding derivatives of the three pigments are identical, within the limits of experimental error. Mixtures of any two of the three oximes or dinitrophenylhydrazones formed by gossypol, gossyfulvin, or dianilinogossypol melt over a wide range. Moreover, the absorption spectra of the di-dinitrophenylhydrazones (Fig. 61) formed by the three compounds differ markedly from each other. Thus, it seems evident that the corresponding carbonyl derivatives are isomeric with each other, as deduced from their origin from closely related compounds, their similarity in elementary composition and dissimilarity in melting point, and their absorption spectra. The original nitrogen-containing groups of gossyfulvin and dianilinogossypol are absent in the carbonyl derivatives. In view of the isomerism of the deriva-

tives, it seems probable that the original nitrogen-containing groups are removed just prior to reaction with the carbonyl reagents, and the substituting groups then enter the molecules in positions differing in the two molecules, and differing from that of the carbonyl groups of gossypol.

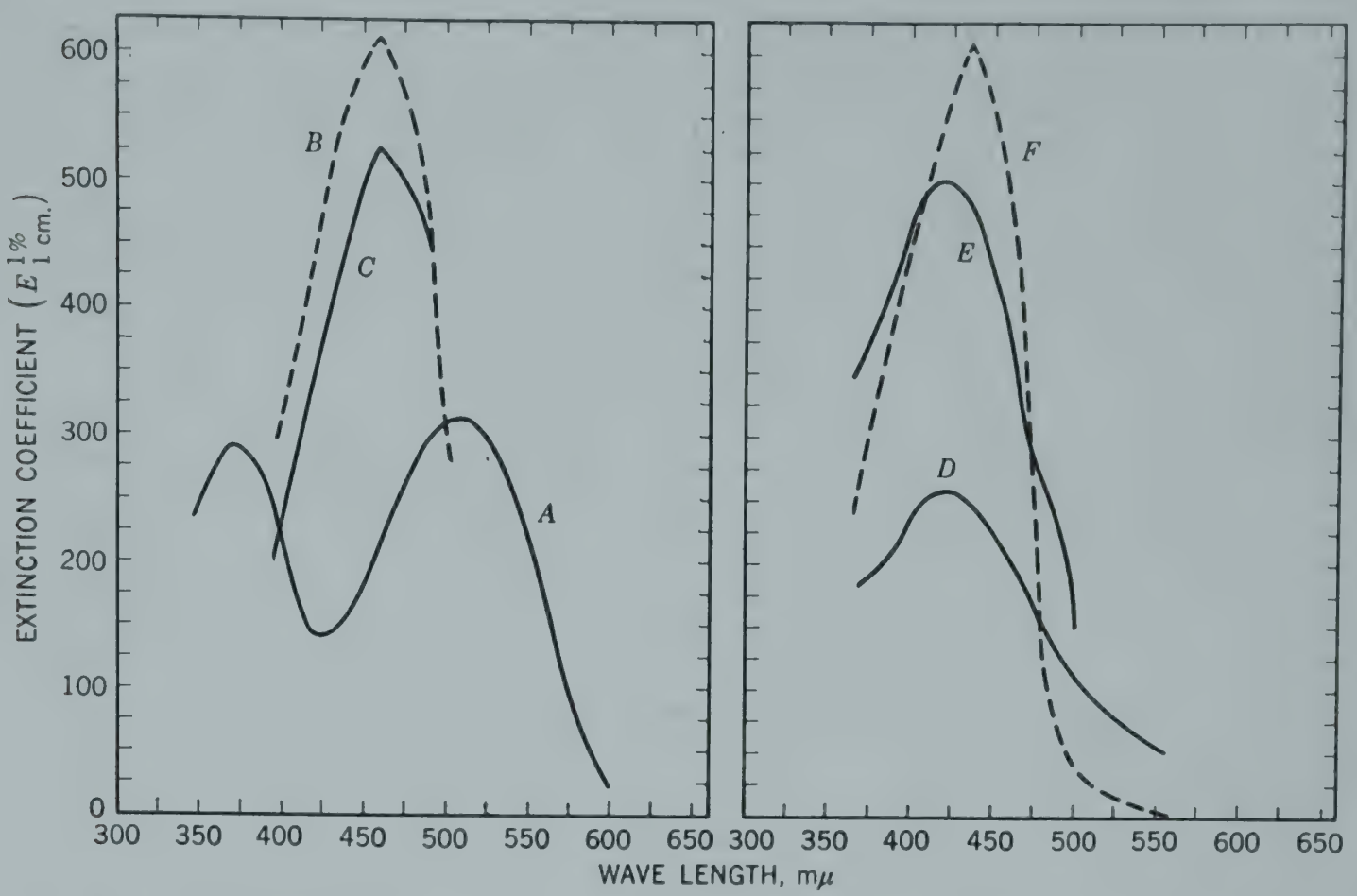


Fig. 61. Absorption spectra of chloroform solutions of the antimony trichloride reaction product of (*A*) gossypol, (*B*) dianilinogossypol, and (*C*) gossyfulvin; and the di-2,4-dinitrophenylhydrazone formed by (*D*) gossypol, (*E*) dianilinogossypol, and (*F*) gossyfulvin.[34]

A further indication of the structural similarity of dianilinogossypol and gossyfulvin and of their differentiation from gossypol is provided by the absorption spectra of the antimony trichloride reaction products of the three compounds (Fig. 61). Gossypol and dianilinogossypol form stable reaction products with antimony trichloride which have different absorption spectra. The curve of the absorption spectrum of the unstable antimony trichloride reaction product formed with gossyfulvin is of a shape similar to that of the dianilinogossypol reaction product, but it is lower.

The color, melting point, and acetyl content of acetylated gossyfulvin suggest that it is identical with the hexaacetoxygossypol which is formed in small amounts upon acetylation of gossypol [50] and as the only product upon acetylation of dianilinogossypol.[48] However, since the gossypol derivatives were not prepared during the investigation in which the gossyfulvin derivative was obtained,[34] direct comparison of the three derivatives cannot be made.

Further information concerning the structural relationship of gos-

sypol, gossyfulvin, and dianilinogossypol has been obtained by a series of qualitative tests carried out simultaneously with these compounds. The results of these tests, as well as the functional groups indicated by analysis of the derivatives described above, are shown in Table 69.

TABLE 69

Reactions of Gossypol, Gossyfulvin, and Dianilinogossypol Based on Their Functional Groups

Group or structure indicated	Reagent used[a]	Gossypol	Gossyfulvin	Dianilino-gossypol
Reducing group	Fehling's Solution	Present	Absent	Present
Oxidizable group	$KMnO_4$	Present	Present	Present
Reactive methylene	$NaOC_2H_5$-$HgCl_2$	Present	Present	Absent
Aliphatic double bond	ICI in HOAc[b]	Absent	Absent	Absent
Phenolic hydroxyl	$FeCl_3$	Blue	Orange	Orange
Phenolic hydroxyl	Ceric nitrate	Present	Present	Present
Carbonyl	Dinitrophenyl-hydrazone	2 present	2 present	2 with loss of aniline
Carbonyl	Hydroxylamine	2 present	2 potential	2 potential
Hydroxyl	Acetic anhydride (NaOAc or pyridine)	4 and 6 present	6 present	4 and 6 present

[a] Methods of Shriner and Fuson, *Identification of Organic Compounds*, 2nd ed., Wiley, New York, 1940, used for all tests, except where otherwise indicated.

[b] American Oil Chemists' Society, *Official and Tentative Methods*, 2nd ed., Chicago, 1946, pp. CD 1–25.

These data indicate that gossypol exists in solution in at least two tautomeric modifications. The preponderant form seems to possess only four hydroxyl and two carbonyl groups instead of six hydroxyl and two carbonyl groups as previously proposed,[72] while the minor form reacts as if it contains six hydroxyl groups.

Acetylation appears to stabilize the two forms, since the hexaacetate and tetraacetate are not interconvertible. On the other hand, the fact that a single product is formed upon acetylation of gossyfulvin and the mode of its reaction with carbonyl reagents indicate that it does not occur in tautomeric modifications, but that it is a derivative of the hexahydroxy tautomer of gossypol containing six hydroxyl groups and no free carbonyl groups. The shift of the absorption bands toward longer wave lengths in dianilinogossypol and gossyfulvin suggests that these compounds contain a more complex system of conjugated double bonds than does gossypol. Furthermore, it appears probable that the additional double bonds result from the formation of enol groups, which are stabilized by their reaction to form nitrogen derivatives.

On the basis of the observations that gossyfulvin has been detected only in seed of high moisture content,[34] and that the pigment gland walls which normally segregate gossypol from other parts of the seed are

particularly susceptible to the action of water,[42] it seems probable that gossyfulvin is formed in cottonseed through the interaction of an enol tautomer of gossypol with the nitrogen-containing groups of proteins or protein fission products of the seed tissue surrounding the pigment glands.

C. Other Pigments of Cottonseed

1. Flavones

Although many of the pigments of the cotton flower have been isolated and identified as flavones,[101] there is little evidence that these or related pigments occur in the seed. Palmer [102] stated that the yellow color of cottonseed meal must be due to gossypetin, one of the flavone pigments found in cotton flowers. However, he appears to have arrived at this conclusion by analogy, since no experimental evidence is cited in its support.

Stanford and Viehoever [12] first suggested that flavones might be present in cottonseed, although no flavones could be detected in the pigment glands. They reported that the formation of a yellow stain with sulfuric acid indicated the possible presence of flavones in the palisade layers of the cotyledons. According to Palmer,[102] Viehoever and Capen reported that quercetin, isoquercetin, quercimeritrin, and gossypetin—which are present in the cotton plant—are absent in the seed. They attributed the previously recorded microchemical reaction with sulfuric acid to the presence of xanthophylls.

Gurevich [103] recently reported additional microchemical tests which suggested the presence of flavones or closely related pigments in the epidermal cells of the cotyledons above the palisade cells and occasionally in the palisade cells. Treatment of sections of cottonseed with ferric choride and potassium dichromate produced a weak stain in the epidermal cells. Treatment of similar sections with either ammonia or sulfuric acid produced a green coloration. The small, yellow, aciculate crystals formed in the cells of the epidermis and palisade layer upon treatment with gaseous hydrogen chloride are characteristic of flavones. However, as pointed out by Gurevich, even though the pigments responsible for these reactions are thus definitely localized, the reactions are not specific for flavones and might be due to chlorogenic acid, which may be a constituent of cottonseed.[104]

[101] J. A. Thorpe and M. A. Whiteley, *Dictionary of Applied Chemistry*, 4th ed., Vol. III, 1939, p. 404.

[102] L. S. Palmer, *Carotenoids and Related Pigments. The Chromolipids*, Chemical Cat. Co., New York, 1922, p. 21.

[103] M. Gurevich, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov*, **1936**, 31–42 (English summary, pp. 41–42).

[104] M. Gurevich cited A. Oparin and S. Rogowin, *Melliand Textilber.*, **11**, 944–946 (1930), who state that K. Gorter, *Arch. Pharm.*, **247**, 184–196 (1909) and A. Oparin,

As pointed out by Goldovskii,[105] before any definite conclusions can be drawn concerning the presence of flavones in cottonseed, the microchemical tests will have to be supplemented by isolation and identification of these pigments.

2. Anthocyanins

Gurevich [103] suggested that the violet "slime" which emanates from the pigment glands of stored cottonseed upon treatment with water might be an anthocyanin-like pigment. Podol'skaia's subsequent investigation [106] of the absorption spectra of aqueous solutions of the red-violet pigment demonstrated the presence of absorption bands at 550 to 570 mμ and at 590 to 625 mμ. These she considered as confirmation of Gurevich's conclusions concerning the anthocyanin nature of the purple water-dispersable pigment of the pigment glands of cottonseed.

It has been reported [29] that the purple suspensions which are formed in aqueous extracts of cottonseed consist of a mixture or chemical combination of protein with gossypol and gossypurpurin. Gossypurpurin has been shown [42] to constitute one of the components of the pigment glands of cottonseed. When water is added to solutions of gossypurpurin in ethanol or dioxane, suspensions of gossypurpurin are formed which have the appearance of a true solution and are blue in color. Spectrophotometric examination of these suspensions has revealed the presence of a broad absorption band having a maximum at 570 mμ and a shoulder at 590 to 620 mμ. Podol'skaia [106] also observed that the amount of the water-dispersable red-violet pigment contained in the pigment glands increases in proportion to the increase in the content of gossypurpurin of the glands.[107] Consequently, it appears probable that the purple streams of finely divided particles which are observed,[42, 103, 106] to emanate from dark red or purple pigment glands upon treatment with water actually represent suspensions of either free or adsorbed gossypurpurin.

3. Carotenoids

Incidental to an investigation of the pigments of butter fat, Palmer and Eckles [108] reported the occurrence of carotene and xanthophylls in cottonseed. On the basis of their chromatographic adsorption charac-

Biochem. Z., **124,** 90–96 (1921), reported chlorogenic acid in cottonseed. However, perusal of these articles reveals no record of the detection of this acid in cottonseed.

[105] A. M. Goldovskii, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1936,** 5–31 (English summary, pp. 28–31).

[106] M. Z. Podol'skaia, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1939,** 61–72 (English summary, pp. 71–72); *Chem. Abst.*, **36,** 7064 (1942).

[107] Podol'skaia reported a concurrent increase of the red-violet pigment and of "red gossypol," but the latter has been shown (see footnote 29) to consist of a mixture of gossypol and gossypurpurin.

[108] L. S. Palmer and C. H. Eckles, *Missouri Agr. Expt. Sta. Research Bull.*, **10,** 339–387 (1914).

teristics and absorption spectra, the carotenoid pigments of cottonseed oil were reported to consist of equal parts of carotene (presumably β-carotene) and a total of five xanthophylls. Carotene was said to be detected in the oil by observation of the absorption bands characteristic of this pigment. A solution of cottonseed oil in carbon disulfide was chromatographed on a column of calcium carbonate. The principal xanthophyll pigment was not adsorbed under these conditions; its absorption spectrum in the effluent from the adsorption column exhibited bands at 238 to 260 mμ, and 285 to 303 mμ, and end absorption at 355 mμ. The other xanthophylls were strongly adsorbed on the column in four bands. They were eluted by 1% solutions of ethanol in petroleum naphtha. No further properties of these pigments were reported by Palmer and Eckles. They attributed the carotenoid content of cottonseed meal and hulls to adhering oil. The observed depletion of carotene in the butter fat produced by cows fed on a diet of cottonseed meal and hulls was attributed by these investigators to the absorption of the carotene by the residual oil in the cottonseed meal, which was assumed to render it unavailable.

A later worker, Gill,[109] was unable to obtain any evidence for the occurrence of carotene in cottonseed meal or oil, by application of a number of qualitative tests developed by Palmer and Eckles.

The detection and isolation of a carotene pigment from cottonseed and cottonseed oil has recently been reported by Podol'skaia.[110, 111] She observed the persistence of a yellow color in ethanol extracts of cottonseed which had been freed of gossypol by treatment with aniline. The yellow color was completely adsorbed on barium hydroxide and could be eluted by washing with ethanol. Since no fractionation could be obtained by distribution of the colored material between aqueous ethanol and petroleum naphtha, and since the absorption spectrum was the same in both solvents, it was concluded that the extract contained a single pigment.

Upon examination of the absorption spectrum of ethanol and petroleum naphtha solutions of the pigment, two bands were observed: one at 450 to 460 mμ, and another more intense band at 470 to 484 mμ. In carbon disulfide solution, the positions of the bands were shifted to 460 to 480 mμ, and 500 to 515 mμ, respectively. The absorption band in the region of shorter wave length was somewhat broader in carbon disulfide than in ethanol or petroleum naphtha solution. Solutions of the yellow cottonseed pigment, like those of carotenoids, were not affected by prolonged exposure to strong alkalies. On the basis of the foregoing properties, Podol'-

[109] A. H. Gill, *Ind. Eng. Chem.*, **10,** 612–614 (1918).

[110] M. Z. Podol'skaia, *Masloboino Zhirovoe Delo,* **13,** No. 6, 8–9 (1937); *Chem. Abst.*, **32,** 4366 (1938).

[111] M. Z. Podol'skaia, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1939,** 83–94 (English summary, p. 94); *Chem. Abst.* **36,** 7064 (1942).

skaia concluded that the yellow cottonseed pigment is either β-carotene or a mixture of closely related carotenoid pigments.

Application of methods developed by Podol'skaia for the quantitative determination of the carotenoid pigment in cottonseed and cottonseed oil is discussed in later sections.

4. Chlorophyll

The presence of small amounts of chlorophyll in cottonseed extracts and oils has occasionally been reported.[112-114] Identification of this pigment has been based on observation of an absorption band at 660 mμ which is characteristic of chlorophyll. Thornton [115] reported the detection of a colorless precursor of chlorophyll in the walls of the protein cells of the seed kernel.

5. Resin Pigments

The dark color of crude cottonseed oil has often been attributed to the presence of resin pigments,[113, 115, 116] and, on the assumption that these pigments occur in the pigment glands, the latter have frequently been called resin glands.[12] However, no experimental data indicating the presence of resin pigments in cottonseed have been published to date.

Recent microchemical investigations [117] have revealed no reactions indicative of the presence of saponifiable resins in the kernels of cottonseed. It has been suggested [117] that the colored acidic components of cooked cottonseed which have previously been mistaken for resin pigments may be decomposition products of gossypol.

6. Pigments of Unidentified Nature

A number of pigments, in addition to those described in the foregoing sections, have been detected in cottonseed or cottonseed products. However, since practically nothing is known concerning the chemistry of these pigments, they will be discussed only briefly in this section.

Podol'skaia [106, 118] reported the presence of several yellow and orange pigments in the pigment glands of cottonseed. The concentration of these pigments was observed to be less in the glands of mature than of immature seed, whereas the content of gossypol and gossypurpurin increased as the seed matured. Consequently, it appeared probable that they were replaced by gossypol and gossypurpurin as the seed matured.

[112] D. Wesson, *Cotton Oil Press,* **6,** No. 5, 33–37 (1922).
[113] G. S. Jamieson and W. F. Baughman, *Oil & Fat Ind.,* **3,** 347–353 (1926).
[114] H. J. McNicholas, *Oil & Soap,* **12,** 167–178 (1935).
[115] M. K. Thornton, Jr., *Oil Miller and Cotton Ginner,* **35,** 11–13 (1929).
[116] G. S. Jamieson and W. F. Baughman, *Oil & Fat Ind.,* **2,** 101–105 (1925).
[117] L. A. Tobler, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1939,** 94–99 (English summary, p. 99); *Masloboino Zhirovoe Delo,* **14,** No. 6, 13 (1938); *Chem. Abst.,* **33,** 5688 (1939).
[118] M. Z. Podol'skaia, *Masloboino Zhirovoe Delo,* **15,** No. 3, 9–10 (1939); *Chem. Abst.,* **34,** 1355 (1940).

Spectroscopic examination of chloroform extracts of immature seed indicated the probable presence of two pigments in addition to gossypol and gossypurpurin. One of these pigments was characterized by the presence of two absorption bands, at 430 to 440 mμ and at 480 to 500 mμ; and the other, by absorption bands at 430 to 440 mμ and 457 to 460 mμ. The ultraviolet absorption spectra of the extracts were similar to that of gossypol. Crystalline products isolated from extracts containing these pigments were reported to exhibit chemical properties identical with those of gossypol.

In an investigation carried out by Boatner and co-workers,[34] fractionation of the orange precipitate obtained from ethereal extracts of cottonseed indicated the presence of one or two orange-colored pigments in addition to gossyfulvin.

The presence of a pale yellow pigment in solution in the oil in the extraglandular tissue of cottonseed was demonstrated [38, 39] by spectrophotometric analysis of petroleum naphtha extracts of cottonseed. The absorption spectrum of this pigment differs from that of any previously isolated cottonseed pigment. The yellow pigment is a nonacidic compound, and is not appreciably affected during alkali refining of solvent-extracted oil.

Spectrophotometric examination [95] of hydraulic- and screw-pressed cottonseed oils and meals indicated the presence of well-defined bands in their respective absorption spectra. Crude hydraulic-pressed oils appear to contain two principal pigments, and screw-pressed oils, one. The corresponding meals appear to contain two each. The absorption spectra of the oils after alkali refining indicate the presence of at least two pigments in hydraulic-pressed oils, and several in screw-pressed oils. It was suggested [95] that most of these pigments are formed from gossypol during cooking of the seed and subsequent expression of the oil.

III. Distribution and Variation of Pigments in the Cottonseed Kernel

The distribution of the more important classes of plant pigments, such as the anthocyanins, flavones, carotenoids, and chlorophylls, in plant tissue follows a rather consistent pattern.[119] Thus, the water-soluble anthocyanins are usually dissolved in the cell sap. The flavones frequently occur as powdery deposits in bark or on leaves, stems, flowers, and seed capsules. The carotenoid and chlorophyll pigments are usually segregated in small, discrete, cellular inclusions designated as plastids.

The pigments of cottonseed are unique with respect to their chemical nature, as well as their distribution in the seed tissue. Most of the pigments are contained in distinct morphological structures, which are relatively large ovoid or spherical bodies, 100 to 400 microns on the long

[119] P. Haas and T. G. Hill, *An Introduction to the Chemistry of Plant Products*. Vol. I, 4th ed., Longmans, Green, New York, 1928.

axis.[12] These pigment-containing structures have been variously referred to as *secretion cavities, resin glands, oil glands, gossypol glands,* and *pigment glands,* of which the last mentioned appears to be the most appropriate.[42] The pigment glands are characteristic of all species of the genus *Gossypium,* and have been reported [12, 13] to be peculiar to this genus and a few closely related genera of the subfamily *Hibisceae.* The structure and properties of the pigment glands appear to be a predominant factor in the development and the variation of the pigments, and are therefore described in some detail here.

A. Types of Pigments

1. Cottonseed Pigment Glands

(a) Formation of the Pigment Gland during the Development of the Seed. Stanford and Viehoever [12] reported that the first sign of the formation of the pigment gland in the embryo appears very soon after fertilization and coincidentally with the differentiation of the tissues of the embryo. A well-defined circle of cells enclosing several other concentrically placed cells (Fig. 62) marks the boundary of the developing gland. Shortly thereafter, a marked change takes place in the center cells; the protoplasm becomes vacuolate and arranged in strands, and is converted into a yellowish, oily appearing substance (Fig. 62 *B* and *C*). These changes are accompanied by a rapid swelling of the cells concerned, some of which are crushed and obliterated in the process, while the peripheral layers become flattened. The nuclei of the swelling cells successively enlarge, degenerate, and disappear. The cell walls usually dissolve and disappear rapidly, leaving the gland as a large central cavity surrounded by layers of flattened cells. This is the appearance of the mature gland.

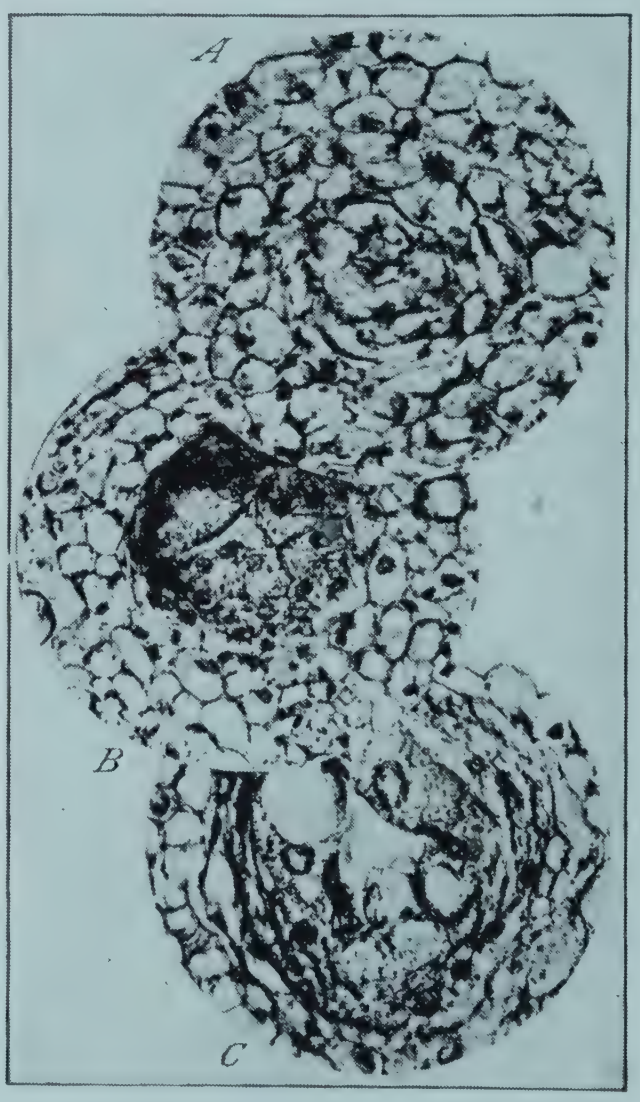


Fig. 62. Cross sections of the developing pigment gland of cottonseed taken from the ovary in the bud, of which *A, B,* and *C* show three stages of its development.[12]

The observations of Stanford and Viehoever concerning the mode of development of the pigment gland were later confirmed by Reeves and

Beasley.[120] The latter investigators reported the first appearance of the pigment gland in the fifteen-day old embryo. It develops rapidly through the sixteenth to eighteenth day, at which time it has attained the structure observed in the mature seed.

(b) Distribution, Shape, and Size. Pigment glands are profusely distributed in the cotyledons and hypocotyls, and are sparsely distributed in the upper part of the radicle, but are usually absent in the tip.[12, 120-122] The glands in the cotyledons are found directly beneath the palisade layer, into which they often project, thus producing a shortening of the palisade cells, but usually no bulging of the outer surface of the cotyledon. The long axis of the pigment gland lies perpendicular to the cotyledon surface. The smaller glands of the radicle are found in the cortex covered by a few parenchymal cells.[12]

The distribution of the glands in the seed tissue, as well as their relatively large and variable size, is illustrated in the photomicrograph in Figure 67a (page 292), showing a cross section of the cottonseed kernel through the cotyledons and radicle. The glands in the inner folds of the cotyledons are smaller than those in the folds near the outer surface of the kernel.

The average size of the glands differs in individual seeds. Examination of relatively large samples of glands obtained by application of the flotation process of separation [41] to a number of seed has confirmed the wide variation in the size of the glands, and revealed a general correlation between their size and shape. Small glands are usually almost spherical, whereas large glands are ovoid.

(c) Structure of the Gland Wall. Von Bretfeld [121] and Hanausek,[122, 123] the earliest investigators of the anatomy of the cottonseed, noted the occurrence of the pigment glands, and reported the existence of a water-sensitive "membrane" enclosing a greenish-black opaque secretion. The "membrane" was described as comprising two layers, with the outer layer being made up of thin-walled, tangentially flattened cells, and the inner layer consisting of a mucilaginized material in which traces of cell walls could be discerned. By successive treatment of the pigment gland with hydrochloric acid, water, and potassium hydroxide, the inner layer was revealed as a yellow, folded, and laminated mass.

More recent investigations [41, 42] have demonstrated that the outer structure of the pigment gland is a more or less rigid wall rather than a membrane. As shown by the photomicrographs in Figure 63, the walls

[120] R. G. Reeves and J. O. Beasley, *J. Agr. Research,* **51,** 935–944 (1935).
[121] von Bretfeld, *J. Landw.,* **35,** 29–56 (1887).
[122] T. F. Hanausek, in J. Wiesner, *Die Rohstoffe der Pflanzenreiches,* Vol. II, 2nd ed., Leipzig, 1903, pp. 754–759.
[123] T. F. Hanausek, *Microscopy of Technical Products,* English translation by A. L. Winton from the German, Wiley, New York, 1907 pp. 362–368.

resist rupture under the pressures applied during flaking of the seed or the violent agitation necessary for detaching the glands from other seed tissue prior to their separation by flotation.[41]

The detailed structure of the gland wall, brought out by successive treatment of the glands with alcoholic acetic acid, aqueous ammonium hydroxide, and water, is illustrated in the photomicrographs in Figure 64. The gland wall is made up of five to eight, closely fitting, thick, curved plates, which are thicker at their centers than at their edges, and are

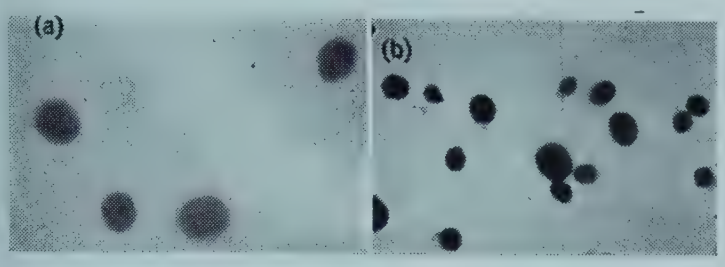


Fig. 63. Photomicrographs of (a) cottonseed flake (×65) and (b) pigment glands separated by flotation from a number of seed (×24).[41]

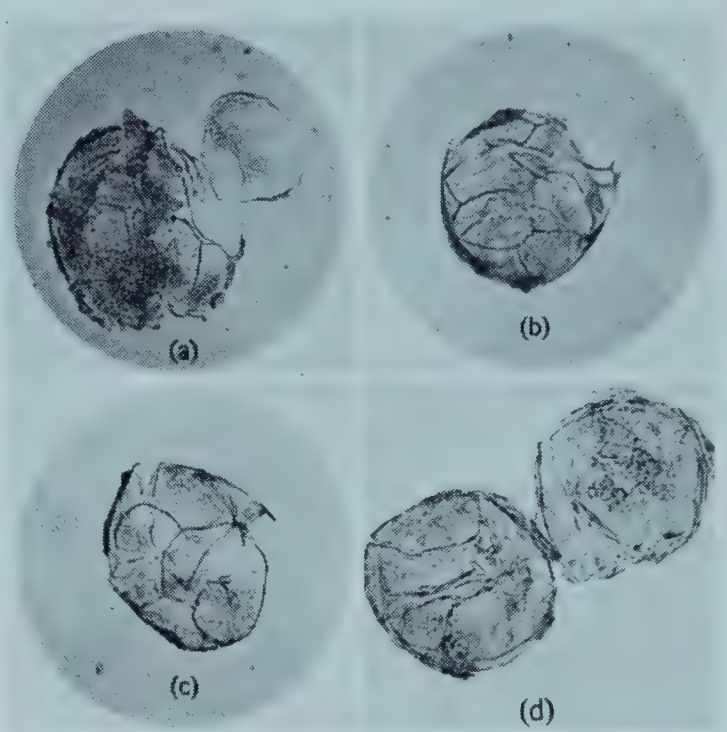


Fig. 64. Photomicrographs (×96) of emptied cottonseed pigment glands, showing wall structure.[42] →

of irregular outline. The seams between the plates are somewhat broader in the treated glands than in the walls of the glands examined in freshly cut sections of seed.

The gland is enveloped in a relatively thick, colorless, transparent layer. This coating is thicker near the centers of the plates than at their edges, so that the outline of the gland is scalloped.

The well-defined circle of cells which is detected in the immature seed prior to the formation of the pigment gland and which persists around the pigment gland of the mature seed has been assumed [12, 123–125] to constitute an integral part of the gland. This does not appear to be true, since intact glands separated from other seed tissue are free of this envelope of cells.[41, 42]

(d) Chemical Composition of the Gland Wall. Microchemical investigation [42] of the emptied pigment gland yielded the results shown in Table 70. Partial solution of the plates composing the gland wall in ammoniacal cupric hydroxide, ammonium oxalate, or dilute sodium hydroxide yielded skeletons which retained the configuration of the original plates.

[124] A. L. Winton and K. B. Winton, *Structure and Composition of Foods,* Vol. I, Wiley, New York, 1932, pp. 552–556.
[125] H. B. Brown, *Cotton,* 2nd ed., McGraw-Hill, New York, 1938, p. 97.

On the basis of the microchemical tests referred to above, it was concluded that the plates are composed of cellulose impregnated with pectin, hemicellulose, and one or more unidentified uronic acid derivatives. The thick transparent material encrusting the glands appeared to consist almost entirely of cutin.

The occurrence in the plates of the gland wall of uronic acid derivatives (which resist solution: by either ammonium oxalate or dilute aqueous alkali) probably accounts for the failure of Gurevich [103] to detect cellulose in the gland.

(e) Physical State of the Gland Contents. Although pigment glands are frequently deeply colored, they appear perfectly clear when viewed

TABLE 70

Microchemical Reactions of Pigment Gland Wall of the Cottonseed[a]

Preparation of glands[b]	Reagent	Observation	Conclusions
None	Millon's reagent	No reaction	Protein absent
None	Phloroglucin and HCl	No reaction	Lignin and pentosan absent
None	Sudan IV	Mottled red stain	Wax, cutin, or suberin present
Hexane washed before emptying	Sudan IV	Mottled red stain	Cutin or suberin present
None	Concd. KOH	Yellow stain	Cutin or suberin present
None	Concd. KOH; heat	Yellow stain	Cutin or suberin present
Heated with concd. KOH	I–$ZnCl_2$	Yellow stain	Cutin present
Alc. HOAc; aq. NH_4OH	Sudan IV	No stain	Cutin removed
" "	Delafield's haematoxylin	Purple stain	Cellulose present
" "	Iodine green	Dark gray-green stain	Impregnated cellulose present
" "	I–KI	Yellow stain	Impregnated cellulose present
" "	I–$ZnCl_2$	Yellow stain	Impregnated cellulose present
" "	Congo red	Yellow-orange stain	Impregnated cellulose present
" "	Ammoniacal $Cu(OH)_2$	Partial solution	Cellulose and hemicellulose dissolved
" "	Ruthenium red	Red stain	Uronic acid derivatives present
None	0.5% $(NH_4)_2C_2O_4$; heated	Partial solution	Pectin removed
Boiled in $(NH_4)_2C_2O_4$	Ruthenium red	Red stain	Uronic acid derivatives present
" " " "	I–$ZnCl_2$	Yellow stain	Impregnated cellulose present
None	Dilute NaOH	Partial solution	Hemicellulose present
Dil. NaOH	Ruthenium red	Red stain	Uronic acid derivatives present
" "	I–$ZnCl_2$	Yellow stain	Impregnated cellulose present

[a] From C. H. Boatner, C. M. Hall, M. L. Rollins, and L. E. Castillon, *Botan. Gaz.*, **108**, 484–494 (1947).

[b] In all cases, the glands were first treated with water to empty them of pigments.

under the microscope in strong light, which suggests that the contents are a homogeneous, single-phase, liquid, or solid solution. When the gland is nicked or broken, its contents are not discharged unless the gland is immersed in water or in an organic liquid in which the pigments are soluble. In the photomicrograph shown in Figure 63b, several fragments of glands can be observed from which the pigments have not been removed even after immersion in the mixture of hydrocarbons used in the flotation process of separating the glands from the remainder of the kernel.

Striations are readily observed (Fig. 65) in cross sections of pigment glands, but examination of a large number of such cross sections reveals no regular arrangement of the striations. These striations have been interpreted by some investigators[12] as vestiges of cell walls within the gland, and by others[42] as fissures in the gelatinous gland contents produced by knife pressure during the cutting of the gland.



Fig. 65. Photomicrograph (×125) of a cross section of cottonseed pigment gland showing striations.[42] (By T. L. W. Bailey and I. V. deGruy.)

The appearance of the mechanically ruptured glands, coupled with their behavior upon contact with water and with organic liquids in which the pigments are soluble, seems to justify the conclusion that the gland contents consist of a gelatinous suspension of solid pigments in a liquid of unknown nature.

(f) Behavior of the Glands toward Various Liquids. *Water.* Von Bretfeld[121] and Hanausek[122, 123] noted that contact of cottonseed pigment glands with water brought about immediate discharge of the contents in the form of a rapidly moving stream of finely divided particles which exhibited lively Brownian movement. Some of the changes which occur during contact with water are illustrated in the photomicrographs in Figure 66, which represent successive photographs of a single pigment gland immersed in water.[42] Examination of the emptied gland (Fig. 66d) shows that the water has removed one of the plates of the gland wall. As may be seen in the photomicrographs of emptied pigment glands (Fig. 64), one or more plates may be either partially or completely detached from the gland wall by the action of water. Contact with any one of a series of saturated aqueous solutions of organic and inorganic compounds produces almost immediate rupture of the gland wall, and the *p*H of the solutions appears to have no effect on the rate of rupture.

The action of water on the glands occurs in several successive steps. Immediately following contact with water, the contents of the glands, which originally appear perfectly clear, become cloudy and lighter in

color, indicating that the entrance of water causes precipitation of the water-insoluble pigments. Immediately following the entrance of water, the pigment contents are expelled through ruptures in the walls in rapidly moving streams of finely divided particles.

Water-Miscible Organic Liquids. Microscopic observation of the effect on cottonseed pigment glands of a series of anhydrous, but water-

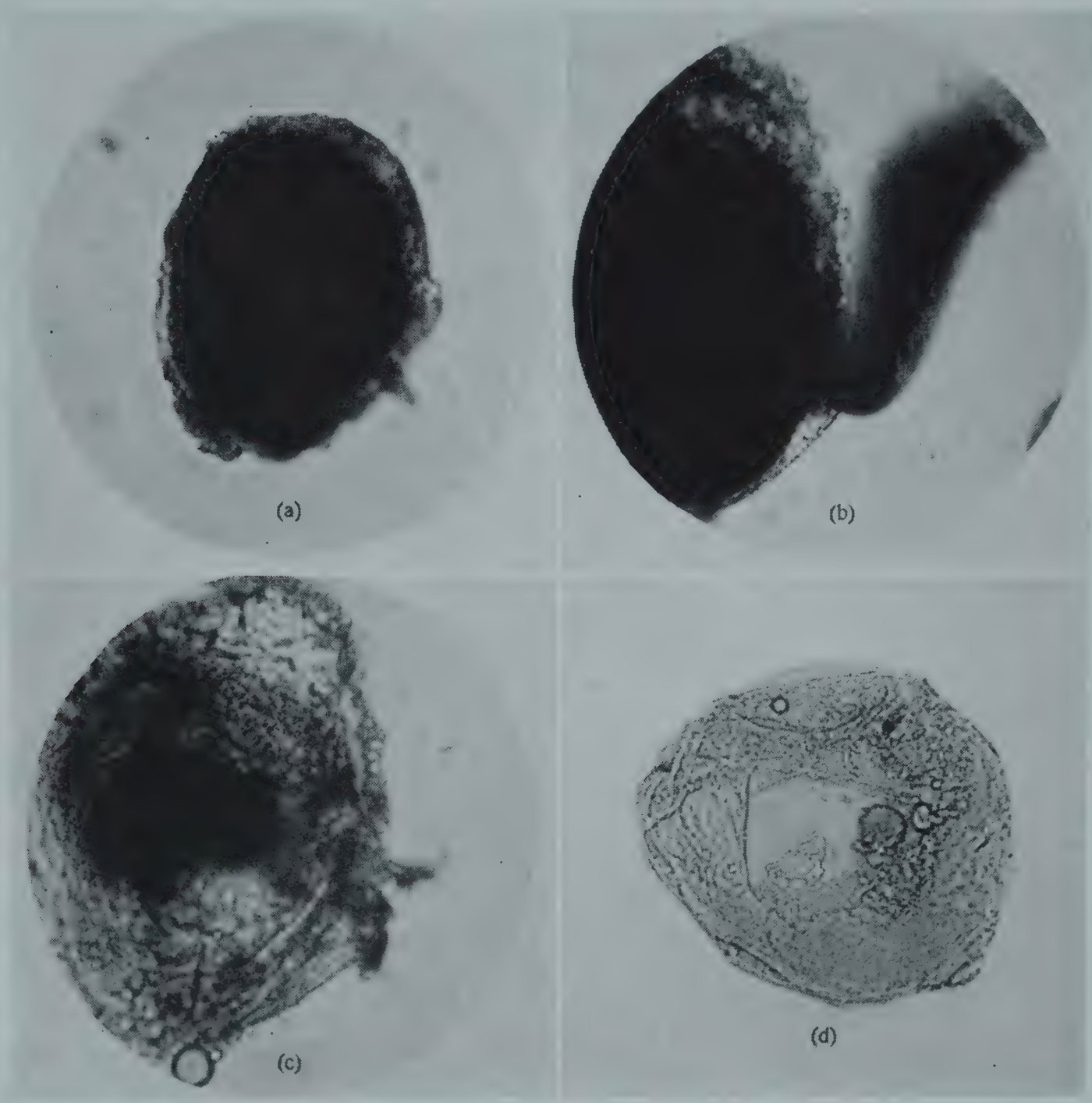


Fig. 66. Photomicrographs (×250) of a cottonseed pigment gland reacting with water: (a) beginning of rupture; (b) gland contents emptying; (c) gland almost emptied; (d) gland completely emptied.[42]

miscible, organic liquids has revealed,[42] as indicated in Table 71, that all of the liquids react with the glands, but less rapidly than water. With mixtures of the organic liquids and water, the glands rupture very much more rapidly, and the speed of rupture increases in proportion to the amount of water contained in the mixture. It can be inferred that the comparative slowness with which anhydrous organic liquids release the pigments from the pigment glands is due to the resistance of the gland wall to attack by these liquids.

TABLE 71

Effect of Water-Miscible Organic Solvents on Cottonseed Pigment Gland[a]

Solvent	Water content, %	Observed reaction of glands
Methanol	0	None ruptured; yellow extract darkening upon longer contact.
	5	Small fraction ruptured after 15 min.; very short purple streams[b]; yellow extract subsequently darkening.
	10	Small fraction ruptured after 10 min.; very slowly moving streams.
	25	Most ruptured after 5 min.; slowly moving streams.
	50	Almost all ruptured immediately; rapidly moving streams.
Ethanol	0	None ruptured; yellow extract darkening upon longer contact.
	5	Small fraction ruptured after 20 min.; pale yellow extract subsequently darkening.
	10	Small fraction ruptured after 10 min.; pale yellow extract subsequently darkening.
	20	Most ruptured after 2–3 min.; very short sluggish streams; yellow extract subsequently darkening.
	50	Most immediately ruptured; rapidly moving streams; yellow precipitate.
Acetone	0	Most ruptured after 10 min.; yellow extract darkening upon longer contact.
	5	Most ruptured after 3–4 min.; yellow extract subsequently darkening.
	10	Most ruptured after 2–3 min.; yellow extract with purple precipitate.
	25	Most ruptured after 1–2 min.; yellow extract with purple precipitate.
	50	Most ruptured immediately; rapidly moving streams.
Dioxane	0	None ruptured; pale yellow extract darkening upon longer contact.
	10	Most ruptured after 4–5 min.; pale yellow extract subsequently darkening.
	25	Most ruptured after 2–3 min.; very few streams.
	50	Most ruptured almost immediately; rapidly moving streams.
Isopropanol	0	None ruptured; pale yellow extract darkening upon longer contact.
	5	Very small fraction ruptured after ½ hr.; yellow extract subsequently darkening.
	10	Small fraction ruptured after 8 min.; yellow extract subsequently darkening.
	20	Most ruptured after 4 min.; yellow extract subsequently darkening.
	50	Most ruptured after 2–3 min.; yellow extract subsequently darkening.
	60	Most ruptured immediately; rapidly moving streams.

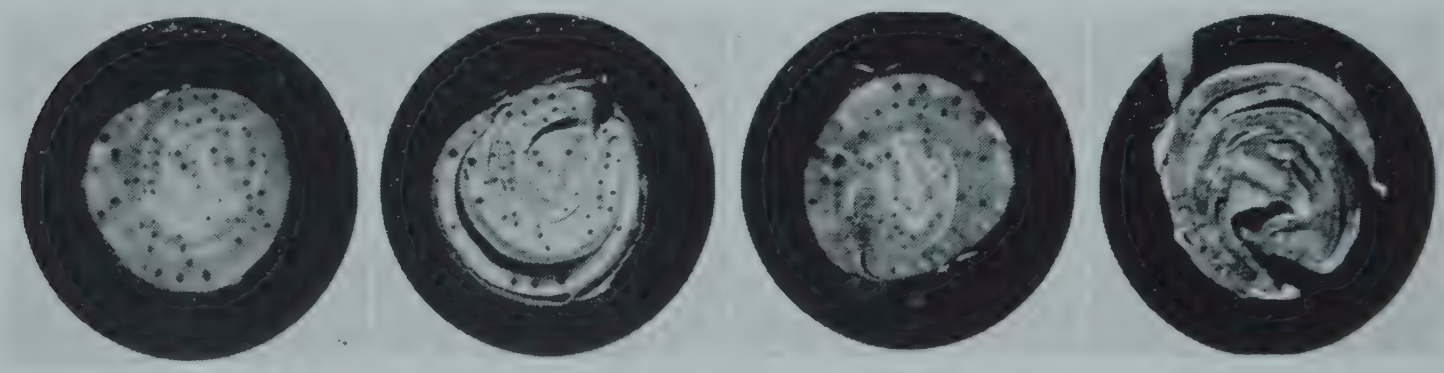
[a] C. H. Boatner, C. M. Hall., M. L. Rollins, and L. E. Castillon, *Botan. Gaz.*, **108**, 484–494 (1947).

[b] "Streams" designates finely divided suspended particles in lively motion emanating from the pigment glands.

It has been reported [37] that gossypol is completely extracted within ten minutes by treatment of finely divided cottonseed with 30% aqueous ethanol, and subsequent addition to the extraction mixtures of 72% aqueous ethanol in such amount as to yield a final solution containing 60% ethanol. The efficacy of this two-step extraction method for the removal of gossypol from cottonseed has been shown [42] to be attributable to rapid rupture of the gland wall by contact with the 30% aqueous ethanol, and subsequent solution of the gossypol suspended in the extract upon addition of the stronger solution.

Rapid extraction of gossypol is also obtained by treating cottonseed with aqueous solutions of other water-miscible organic liquids, such as acetone, methanol, 1,4-dioxane, and isopropanol.[39] Preliminary wetting of the meal, followed by addition of a water-miscible organic liquid in which the pigment is soluble, yields similar results.

Other Organic Liquids. Organic liquids other than water-miscible ones of low molecular weight have been found [41] to fall into two categories with respect to their activity toward the glands: (*a*) those having little or no effect on the glands even after contact for twenty-four hours, and (*b*) those which completely extract the gossypol from the glands after contact for twenty-four hours or less. The *inert* group includes solvents such as hydrocarbons, chlorinated hydrocarbons, and triglycerides. The *active* group includes chloroform and diethyl ether. The appearance of the pigment glands after contact for 24 hours with petroleum naphtha (Skellysolve F) and with diethyl ether is shown by the photomicrographs of cross sections of cottonseed (Fig. 67).



(a) (b) (c) (d)

Fig. 67. Photomicrographs (×3.5) of transverse sections of cottonseed: (a) freshly cut section and (b) same section after immersion in Skellysolve F for 24 hours; (c) freshly cut section and (d) same section after immersion in diethyl ether for 24 hours.[41]

It has been observed [42] that preliminary drying of ether or chloroform reduces the effectiveness of these solvents for extracting gossypol from cottonseed. However—when the separated pigment glands are first macerated with sharp sand, or the separated pigment glands or finely divided seed are first moistened with water in order to rupture the gland

walls—the pigment contents are rendered instantly soluble in either chloroform or ether.

Thus, it appears that the pigments contained in the glands will remain largely unaffected until the walls have been ruptured, but will be extracted thereafter by any solvent in which they are soluble. Solvents which are themselves incapable of attacking the glands may effect rupture after prolonged contact because of their slight moisture content.

(g) Relation of the Gland Walls to the Distribution and Variation of Cottonseed Pigments. By analogy with their behavior in thin sections and flakes of cottonseed, it appears probable that the gland walls serve in a protective capacity for the preservation of the very active and unstable polyphenolic pigments in the glands. Also, it may be presumed that, unless other as yet unrecognized protective mechanisms are operative in the seed kernel, the pigments occurring in solution in the fluids of the extraglandular tissue are relatively stable and nonreactive.

It has not yet been possible to demonstrate that any interchange occurs between the material contained in the gland and in the surrounding tissue, and it has generally been inferred [124, 125] that the pigment glands are purely excretory organs in which the pigments are deposited as metabolic byproducts during development of the seed. However, observed variations in the gland pigments during storage of cottonseed [106, 118] are difficult to explain on the assumption that there is no transfer of material across the gland walls. This is particularly true of the observation that gossypol decreases and gossypurpurin increases during storage of mature cottonseed, since gossypol contains no nitrogen, whereas nitrogen appears to constitute an intrinsic part of the gossypurpurin molecule.

Although no direct evidence is as yet available on the point, it seems probable that certain transformations occurring in moist seed during storage can be attributed to the action of water on the gland wall.

2. Intraglandular Pigments

Even casual examination of a section of cottonseed reveals the fact that most of the deeply colored pigments of the seed are concentrated in the pigment glands. The oil and extraglandular tissue of sound cottonseed are colored a faint yellow, whereas the color of the glands may vary from yellow, through various shades of orange and red to dark purple.[126]

(a) Gossypol and Gossypurpurin. More accurate information concerning the localization of the seed pigments in the glands has been obtained by mechanically separating the glands from the remainder of the seed and comparing the absorption spectra of chloroform extracts of the two fractions (Fig. 68). The difference in the intensity of light absorp-

[126] Increasingly dark colors indicate the presence of increasing proportions of gossypurpurin.

tion of these extracts indicates that most of the pigments of the seed are concentrated in the glands.

Analysis of the absorption spectra of chloroform extracts of a series of samples of pigment glands has shown [39] that gossypol constitutes the principal pigment of the glands, and that gossypurpurin is the only other pigment which is present in detectable amounts. The gossypol content of the chloroform extracts of the pigment glands was determined by the antimony trichloride spectrophotometric method,[127] and the extinction coefficients at different wave lengths were calculated for the absorption due to the presence of gossypol in the extracts. The curves constructed from these calculated values are identical with those experimentally determined with corresponding gland extracts throughout the wave length region (250 to 430 mμ) in which gossypol exhibits selective absorption (see Fig. 44, page 252). Curves of the complete ultraviolet and visible absorption spectra from 240 to 600 mμ of extracts of the pigment glands were found to be composites of the absorption attributable to the content of gossypol and gossypurpurin.

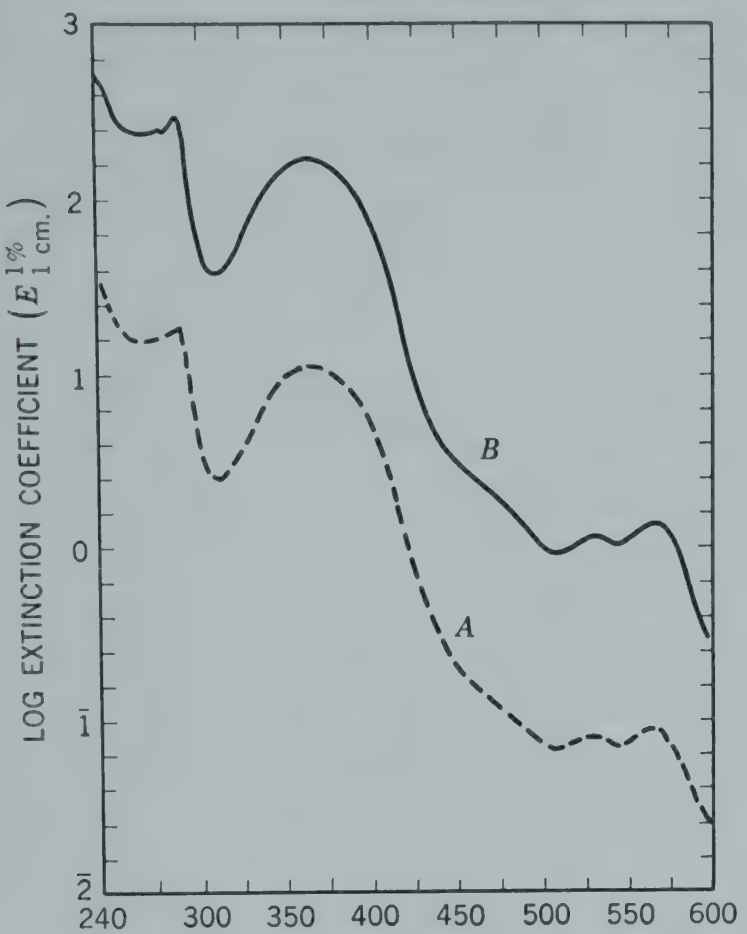


Fig. 68. Absorption spectra of chloroform extracts of (*A*) seed kernels and (*B*) pigment glands separated from the kernels.[39]

As may be seen from the data in Table 72, gossypol has been observed to constitute from 20.6 to 39.0%, and gossypurpurin from 0.471 to 1.35% of the weight of the pigment glands obtained from different samples of cottonseed. Although there is a rather wide variation in the gossypol and gossypurpurin contents of glands in different seeds, a general correlation can be observed between the weight of the glands and the weight of the afore-mentioned pigments in a given variety of seed (Table 72). The percentage by weight of glands in the seed kernels, calculated on the basis of observed contents of gossypol in the kernels and the corresponding glands, varies from 2.37 to 4.81%.

Smirnova [15] noted the existence of a general correlation between the number of glands and the gossypol content of a wide selection of varieties

[127] C. H. Boatner, M. Caravella, and L. Kyame, *Ind. Eng. Chem., Anal. Ed.*, **16**, 566–572 (1944).

TABLE 72

Comparison of Gossypol and Gossypurpurin Content of Entire Seed Kernels and of Corresponding Pigment Glands[a]

Sample variety	Gossypol content, %[b]	Gossypurpurin content, %[c]	Weight of glands in seed kernels, %[d]
(1) Delfos 651[e]	1.09	0.055	2.66
(2) Pigment glands from (1)	40.9	1.73	—
(3) Cleve Wilt[f]	2.39	0.0388	4.81
(4) Pigment glands from (3)	49.2	0.612	—
(5) D & PL–45[g]	1.14	0.0368	2.92
(6) Pigment glands from (5)	39.0	1.08	—
(7) Delfos–451–42–43[h]	1.11	0.0286	2.37
(8) Pigment glands from (7)	43.96	1.081	—

[a] C. H. Boatner, C. M. Hall, R. T. O'Connor, and L. E. Castillon, *Botan. Gaz.*, **109**, No. 2 (Dec., 1947).

[b] Determined by application of antimony trichloride spectrophotometric method. C. H. Boatner, M. Caravella, and L. Kyame, *Ind. Eng. Chem., Anal. Ed.*, **16**, 566–572 (1944).

[c] Calculated on Basis of $E^{1\%}_{1\ cm.}$ of chloroform extract and $E^{1\%}_{1\ cm.}$ of pure gossypurpurin = 225.7 at 565–566 mμ. C. H. Boatner, C. M. Hall, R. T. O'Connor, and L. E. Castillon, *J. Am. Oil. Chem. Soc.*, **24**, 97–106 (1947).

[d] Calculated on basis of gossypol content of glands and corresponding seed.

[e] Pure-bred cottonseed from 1943 crop at Stoneville, Miss., stored 2 years prior to separation of glands.

[f] Pure-bred cottonseed from 1943 crop at Clemson, S. C., stored 2 years prior to separation of glands.

[g] Pure-bred cottonseed from 1944 crop at Stoneville, Miss., stored 2½ years prior to separation of glands.

[h] Pure-bred cottonseed from 1945 crop at Stoneville, Miss., stored 1½ years prior to separation of glands.

TABLE 73

Relation between Number of Glands and Gossypol Content of Cottonseed[a]

Species of *Gossypium*	Strain	Number of glands in seed sections			Gossypol (dry weight), %[b]
		Least	Most	Average	
herbaceum	2270	9	43	23	0.15
herbaceum	101	8	32	21	0.46
hirsutum	1306	15	56	36	0.51
hirsutum	169	27	56	35	0.57
hirsutum	13714	15	49	30	0.74
hirsutum	182	27	58	38	0.80
barbadense	924	47	90	68	1.01
hirsutum	915	34	59	45	1.24
barbadense	0671	30	66	46	1.26
hirsutum	14848	42	81	56	1.31
—	928	40	69	58	1.53
—	19153	37	75	52	1.59

[a] M. I. Smirnova, *Bull. Applied Botany Genetics Plant Breeding U.S.S.R.*, **Ser. III**, No. 15, 227–240 (1936) (English summary, p. 240).

[b] Determined by modification of method of F. E. Carruth, *J. Biol. Chem.*, 32, 87–90 (1917).

and strains of cottonseed (Table 73). On the basis of this observed correlation, it was pointed out that counting the glands in sections of seeds would provide a convenient and rapid means for determining the approximate gossypol content of the seed. More reliable results might be obtained by counting the glands in thin cottonseed flakes, thus reducing the error due to the uneven distribution of the glands in different parts of the embryo.

(b) Other Pigments in the Glands. Incontrovertible evidence for the presence of a given pigment in the glands of cottonseed can be obtained only by its isolation therefrom and subsequent identification. A practical process for the separation of pigment glands in quantities sufficient for accurate identification of their pigments has been developed only recently, so that only a limited number of samples of pigment glands have been investigated. Only gossypol and gossypurpurin were detected in these glands.[39]

In the absence of more direct evidence, deductions with respect to the localization of other pigments have been based on visual observation of the colors of the glands, or observations of the relative difficulty with which a given pigment is extracted from cottonseed.

Orange and Yellow Pigments of Immature Cottonseed. Podol'skaia [106, 118] reported the occurrence of yellow and orange-yellow pigments in the pigment glands of immature cottonseed. Her conclusions concerning the localization of these pigments were based presumably on observation of the colors of the glands, since no other experimental evidence was presented.

Anthocyanin Pigment. Gurevich [103] reported that purple suspensions emanated from purple-colored pigment glands which were brought into contact with water. Podol'skaia [106, 118] later identified this water-dispersible purple pigment as an anthocyanin, on the basis of the absorption spectra of its aqueous solution. However, as has already been pointed out, it is probable that the pigment reported by these investigators represented a mixture of gossypol and gossypurpurin in colloidal suspension.

Gossyfulvin. Gossyfulvin has not been detected in any of the extracts of separated pigment glands which have been examined to date, and it does not, in fact, appear to occur in many samples of cottonseed. However, since prolonged contact of cottonseed with chloroform or ether is required for the complete extraction of gossyfulvin, it is probable that this pigment occurs in the glands rather than in the surrounding tissue.

3. Extraglandular Pigments

A small fraction of the pigment glands is always broken during flaking or grinding of cottonseed; moisture in the seed increases the susceptibility of the glands to mechanical rupture. It is, therefore, not possible to

avoid extraction of some of the pigments of the glands with solvents that are, in themselves, incapable of attacking the pigment glands. But, when extraction is carried out in the absence of excessive amounts of moisture in the seed or solvent, extracts obtained with solvents which do not affect the glands (*e.g.*, petroleum naphtha) contain principally the oil and oil-soluble components of the extraglandular tissue.

(a) Carotenoid Pigments. The oil-soluble carotenoid pigment reported by Podol'skaia [110, 111] was first detected in cottonseed oil obtained by pressing finely ground cottonseed without preliminary cooking. It might, therefore, be inferred that this pigment is a native pigment of the seed, which occurs in solution in the oil of the seed tissue. The pigment is also completely extracted from cottonseed by petroleum naphtha.

Application of a spectrophotometric method developed for the determination of the concentration of this pigment in extracts of cottonseed has shown that its concentration varies from 0.096 to 0.219% in different samples of cottonseed. The content of the carotenoid pigment was found to be greater in immature than in mature seed, but it was present in all expressed and solvent-extracted cottonseed oils which were examined.

(b) Yellow Oil-Soluble Pigment. Spectrophotometric examination of petroleum naphtha extracts of cottonseed has shown that a yellow, noncarotenoid, oil-soluble pigment is present in the extraglandular tissue.[39] The absorption spectrum of this pigment (Fig. 69) differs from that of gossypol, gossypurpurin, or the oil-soluble carotenoid pigment reported by Podol'skaia. It does not react with $SbCl_3$, and is, therefore, readily distinguishable from gossypol in extracts of cottonseed which contain both of these pigments. As may be seen in Figure 70, the difference in the absorption spectrum of a chloroform extract of cottonseed and the absorption spectrum due to gossypol in the extract is equivalent to the absorption spectrum of the yellow, oil-soluble pigment.

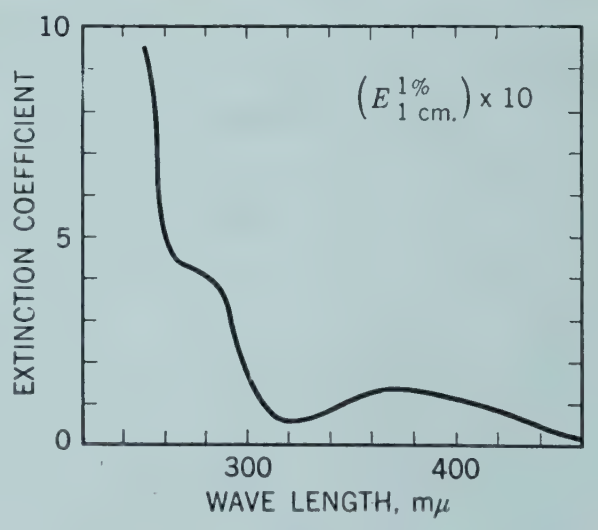


Fig. 69. Absorption spectrum of petroleum naphtha extract of cottonseed containing oil-soluble extraglandular pigment.[39]

The yellow extraglandular pigment is nonacidic, hence it is not extracted from its solutions in organic solvents by treatment with aqueous alkali. Both gossypol and gossypurpurin are quantitatively extracted from such solutions.[38, 39] The observation that all of the pigments are removed by alkaline extraction of chloroform extracts of pigment glands has been proposed as evidence for the absence of the oil-soluble yellow pigment in the pigment glands. However, in extracts containing appreciable amounts of gossypol, the extraglandular pigment has

been detected[38] by examination of the absorption spectrum of the extrac before and after treatment with aqueous alkali (Fig. 71).

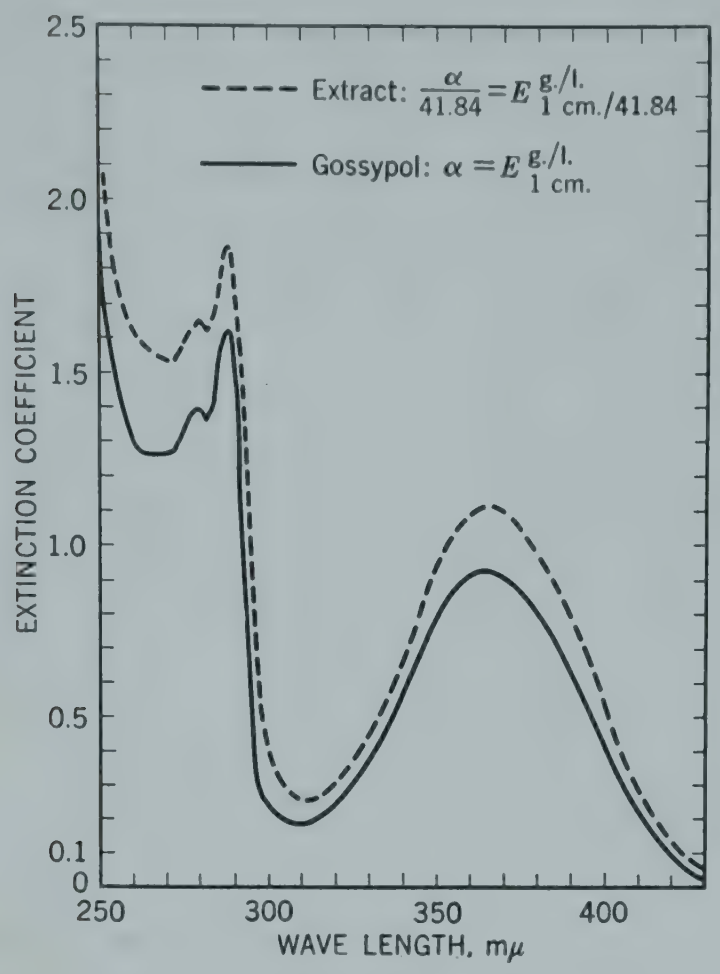


Fig. 70. Absorption spectra of chloroform extract (----) of cottonseed and gossypol (—) in the extract, showing absorption due to presence of oil-soluble extraglandular pigment in the extract.[39]

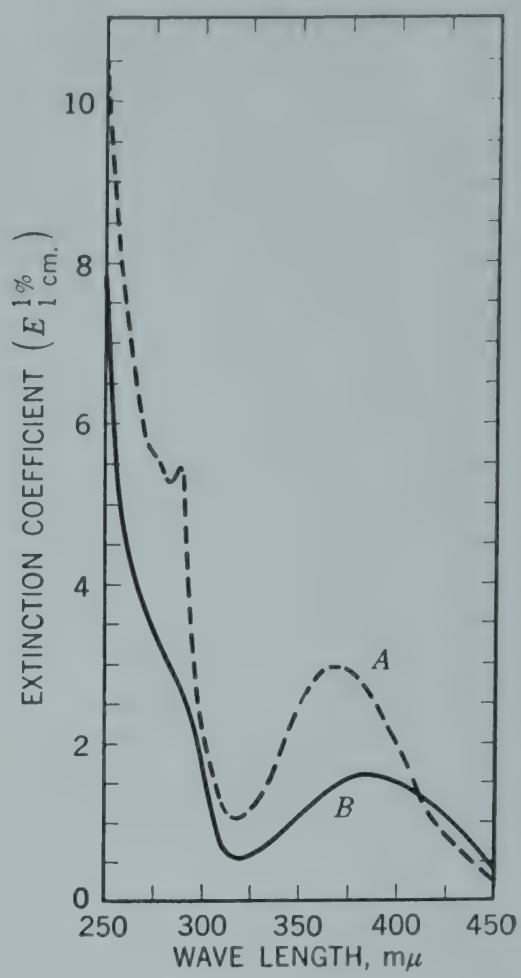


Fig. 71. Absorption spectra of (*A*) petroleum naphtha extract of cottonseed containing appreciable amounts of gossypol and (*B*) this extract after removal of gossypol by alkaline extraction, leaving oil-soluble extraglandular pigment.[38]

(c) Flavone Pigment. A pale yellow pigment has been observed[12, 103] in the epidermal cells of the cotyledons above the palisade cells, and sometimes in the palisade cells. On the basis of the colors which this pigment forms with sulfuric acid, ammonia, and ferric chloride and potassium dichromate, and the yellow crystals observed upon contact with gaseous hydrogen chloride, it has been tentatively identified as a flavone.[12, 103]

(d) Chlorophyll. Thornton[115] reported that a colorless form of chlorophyll occurs in the walls of the protein cells of the seed kernel.

Thus, it would appear that the localization of all of the pigments of the cottonseed kernel has been tentatively established. However, it is quite possible that the cottonseed kernel contains pigments in addition to those which have been detected.

B. Determination of Pigment Content of the Cottonseed Kernel

Accurate estimation of any organic constituent of a plant or animal organism is always accompanied by many difficulties, among which are

the securing of representative samples, complete separation of the constituent from associated materials, and selection of a specific reagent. All of these difficulties are inherent in methods for the determination of the cottonseed pigments.

Sampling of undelinted seed presents a difficult problem. This is particularly true of the large and heterogeneous mixtures of seed processed at oil mills. Samples of such seed obtained by repeated quartering according to the technique recommended for obtaining representative samples for grading [2, 3] do not yield reproducible values for their content of pigments.

The selection of a satisfactory method for extraction of the intraglandular pigments is difficult because of the resistance of the gland walls to solvents. Most organic solvents rupture all of the gland walls only after prolonged contact during which time the extracted pigments may undergo various degrees of decomposition. It is then difficult to differentiate between incompleteness of extraction and decomposition of the extracted pigments due to prolonged contact with the solvent. Therefore, satisfactory methods must be such that extraction is complete within a short time, or the extraction must be carried out under such conditions that there is no appreciable destruction of the extracted pigment.

The chemical similarity of a number of the cottonseed pigments introduces further difficulties in the development of analytical methods which are both complete and specific for a given pigment. It is difficult to establish the completeness of the analytical reaction, since the unstable pigments may undergo simultaneous decomposition and reaction. Consequently, only very rapid reactions and preferably those not requiring elevated temperatures can be employed for the accurate determination of the more unstable pigments.

1. Estimation of Intraglandular Pigments

(a) Gossypol. Numerous articles have been published which deal with the determination of gossypol in cottonseed and cottonseed products. Nearly all of the analytical methods are based on the extraction of gossypol from the seed or meal with diethyl ether, and its subsequent determination in the form of dianilinogossypol. The multiplicity of modifications of this method which have been proposed suggests that none of them is entirely satisfactory.[128]

Extraction from Cottonseed. Schwartze and Alsberg [129] reported that gossypol could be completely extracted from ground cottonseed kernels by exhaustive treatment with diethyl ether in a Soxhlet apparatus. Extrac-

[128] See Reports of Gossypol Committee, American Oil Chemists' Society, *Oil & Soap,* **23,** 235–236 (1946); *J. Am. Oil Chem. Soc.,* **24,** 269–271 (1947).

[129] E. W. Schwartze and C. L. Alsberg, *J. Agr. Research,* **25,** 285–295 (1923),

tion was considered complete when a yellow color could no longer be observed in the ether remaining in contact with the seed in the extractor overnight. These investigators reported that the period required for complete extraction of gossypol from cottonseed varies from twenty-four to seventy-two hours.

Application of this method by Halverson and Smith [130-132] for the extraction of gossypol from cottonseed meal revealed that the pigment is unstable in the ethereal extract during prolonged heating, unless special precautions are observed to stabilize it. These investigators reported that the use of peroxide-free diethyl ether containing small amounts of ethanol and water assists in the extraction of gossypol from the seed and meal, and minimizes its subsequent decomposition.

Complete extraction of gossypol has been obtained [46] from samples of finely ground or flaked cottonseed by equilibration with diethyl ether or chloroform at 3.3° C. for twenty-four hours. No decomposition of gossypol was observed to occur in these extracts when they were stored at 3.3° C. for periods as long as forty-eight hours.

The use of aqueous ethanol and diethyl ether has recently been reported [37] to yield complete extraction of gossypol from cottonseed and cottonseed meal within ten minutes. The extraction is carried out in a Waring Blendor with a mixture of 60% aqueous ethanol and diethyl ether, containing 15 ml. of ether per 75 ml. of aqueous ethanol. The use of the Waring Blendor eliminates the necessity of preliminary grinding or flaking of the seed. However, if finely ground or flaked seed is available, simple equilibration of these materials with aqueous ethanol effects complete extraction of gossypol within ten minutes without the use of a Waring Blendor or the addition of ether.[39, 42] Preliminary treatment of the seed with 30% aqueous ethanol effects immediate rupture of the pigment glands, and the suspended gossypol is then brought into solution by addition of sufficient alcohol to yield a final extract containing 60% ethanol.

Extraction from Cooked Cottonseed Meal. The methods which have been reported for the extraction of gossypol from cooked cottonseed meal are similar to those recommended for the unprocessed seed. Halverson and Smith [130-132] have reported a series of investigations on the effect of different impurities in diethyl ether used for the extraction of gossypol from cottonseed meal. They concluded that there is no definite limit between *free* and *bound* gossypol in cooked cottonseed. They recommend: prior addition of water in amounts up to 20% by weight of the meal; the use of a peroxide-free ether containing small amounts of ethanol, and

[130] J. O. Halverson and F. H. Smith, *Ind. Eng. Chem., Anal. Ed.*, **5**, 320–322 (1933).
[131] J. O. Halverson and F. H. Smith, *Ind. Eng. Chem., Anal. Ed.*, **6**, 356–357 (1934).
[132] J. O. Halverson and F. H. Smith, *Ind. Eng. Chem., Anal. Ed.*, **9**, 516–517 (1937).

water added in excess of its solubility therein; and extraction at elevated temperatures for seventy-two hours.[132] The use of the diethyl ether–ethanol–water mixture recommended by Halverson and Smith has also been reported to effect extraction of gossypol from cottonseed meal when extraction is carried out for seventy-two hours in a Butt-type extractor.[28] Podol'skaia [133–135] reported complete extraction of gossypol from cottonseed meal with diethyl ether after five to ten hours. It has also been reported [46] that gossypol can be completely extracted from cottonseed meal by equilibration with diethyl ether or chloroform for twenty-four hours at 3.3° C.

Treatment with a mixture of aqueous ethanol and ether in a Waring Blendor has been reported [37] to be equally effective for the extraction of gossypol from both cottonseed and cottonseed meal.

Extraction from Defatted Cottonseed. Hydrocarbon solvents extract little gossypol from cottonseed because of their inability to rupture the pigment glands, and the limited solubility of gossypol in these solvents. Moreover, most of the gossypol which is discharged from such glands as are ruptured during grinding or flaking of the seed, defatting, and subsequent drying of the meal, is strongly adsorbed on the protein tissue of the seed. Solvents such as chloroform and diethyl ether have been found [127] to produce erratic and incomplete extraction of the residual gossypol of defatted cottonseed. However, the use of mixtures of water with low molecular weight, water-miscible organic liquids, such as methanol, ethanol, acetone, or dioxane will accomplish complete extraction of the gossypol remaining in the glands, as well as that adsorbed on the tissue.[39]

Extraction from Extracts of Cottonseed and Cottonseed Meal, and from Solutions of Cottonseed Oil. A method has recently been described [95] for the isolation of gossypol in the form of its water-soluble sodium salt from extracts or solutions in water-immiscible organic solvents which contain considerable quantities of other pigmented substances. The extraction is carried out with dilute aqueous sodium hydroxide to which sodium dithionite is added to prevent oxidative decomposition of the sodium gossypolate. For quantitative estimation, the gossypol is subsequently transferred to a suitable organic solvent by acidification of the aqueous extract in contact with the organic solvent.

Application of this method has been reported [95] to permit differentiation of gossypol from its conversion products in cooked cottonseed meal and hot-pressed oils.

[133] M. Z. Podol'skaia and M. Sserga, *Masloboino Zhirovoe Delo,* **10,** No. 7,.19–21 (1934); *Chem. Zentr.,* **II,** 4036 (1934).

[134] M. Z. Podol'skaia, *Masloboino Zhirovaya Prom.,* **16,** No. 5–6, 48–50 (1940); *Chem. Abst.,* **35,** 6137 (1944).

[135] M. Z. Podol'skaia, *J. Applied Chem. U.S.S.R.,* **17,** 657–658 (1944); *Oil & Soap,* **23,** 132 (1946).

Gravimetric Methods for Estimation. All of the gravimetric methods which have been proposed for the quantitative determination of gossypol in cottonseed extracts are based on the formation of dianilinogossypol, which is thermally stable and is relatively insoluble in most organic solvents. The use of dianilinogossypol was first proposed by Carruth [47] for the determination of *bound* gossypol in cooked cottonseed meal. Schwartze and Alsberg [129] applied the method of Carruth to the determination of the gossypol content of cottonseed kernels.

Because of the extreme slowness with which dianilinogossypol precipitates from mixtures containing appreciable amounts of cottonseed oil, methods for acceleration of its precipitation have been investigated. Royce and co-workers [27, 136, 137] found that the addition of pyridine to such extracts (prior to the addition of aniline) yielded more rapid formation of a precipitate. Gossypol precipitates as dianilinodipyridylgossypol,[26, 27] from which the pyridine is completely removed by heating the precipitate at 100° C. for a period of nine hours.[27] The gossypol is estimated on the basis of the weight of dianilinogossypol thus obtained.

Halverson and Smith [138, 139] reported a method for the determination of gossypol in which ethylene glycol is added to extracts of cottonseed meal to accelerate the precipitation of dianilinogossypol.

Spectrophotometric Methods for Estimation. Two of the three spectrophotometric methods which have been proposed for the quantitative determination of gossypol in extracts of cottonseed and cottonseed meal are based on the measurement of the absorption spectrum of dianilinogossypol produced *in situ.*

Lyman, Holland, and Hale[28] reported that dianilinogossypol is rapidly formed when aniline is added to a dilute solution in *n*-butanol of the residue obtained by evaporation of an ethereal extract of cottonseed or cottonseed meal. After twenty minutes, the transmission of the reaction mixture at 440 mμ (Fig. 72) is read against the appropriate blank, which consists of a solution of an aliquot of the ethereal extract in *n*-butanol. The gossypol content of a given extract is calculated by reference to a standard transmittance curve established with pure gossypol. These investigators did not compare the results obtained by their method with those obtained by the gravimetric method, since they were unable to obtain replicate results by the latter method.

Smith [37] has reported a modification of the dianilinogossypol spectrophotometric method in which dianilinogossypol is formed by heating a mixture of aniline and an aqueous ethanol–diethyl ether extract of cottonseed or cottonseed meal. In Figure 73 are reproduced his curves of the

[136] H. D. Royce, *Oil & Soap,* **10,** 183–185 (1933).
[137] H. D. Royce and M. C. Kibler, *Oil & Soap,* **11,** 116, 118–119 (1934).
[138] J. O. Halverson and F. H. Smith, *Ind. Eng. Chem., Anal. Ed.,* **5,** 29–33 (1933).
[139] F. H. Smith, *Ind. Eng. Chem , Anal. Ed.,* **9,** 517–518 (1937).

absorption spectra of the aniline reaction product obtained with extracts of cottonseed and cottonseed meal, and with pure gossypol. The transmission of the reaction mixture at 445 mμ is read against an appropriate blank consisting of corresponding solutions of the extract containing no aniline. The gossypol content is calculated on the basis of the extinction

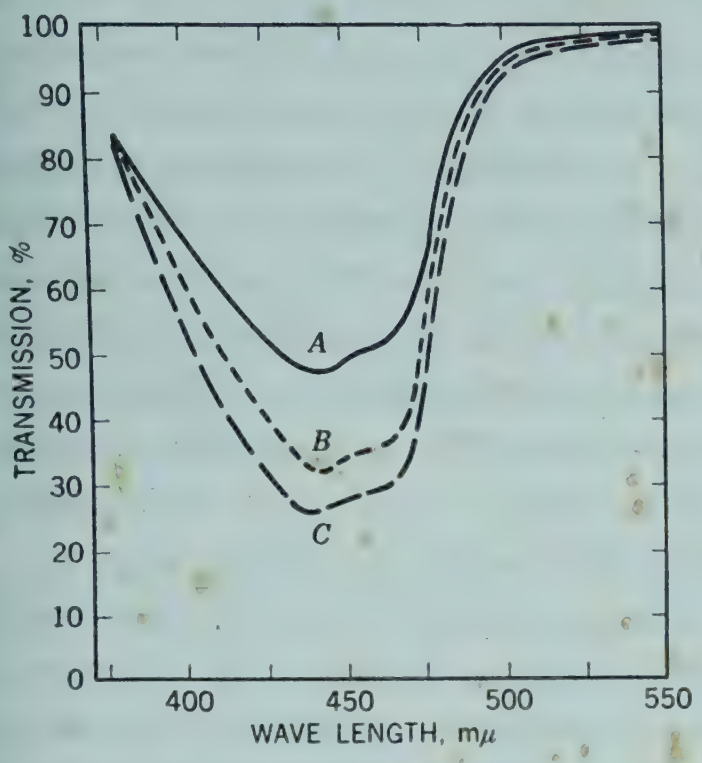


Fig. 72. Transmission spectra in *n*-butanol of aniline reaction product of (*A*) pure gossypol, 0.008% solution; (*B*) diluted ether extract of cottonseed meal; and (*C*) pure gossypol, 0.016% solution.[28]

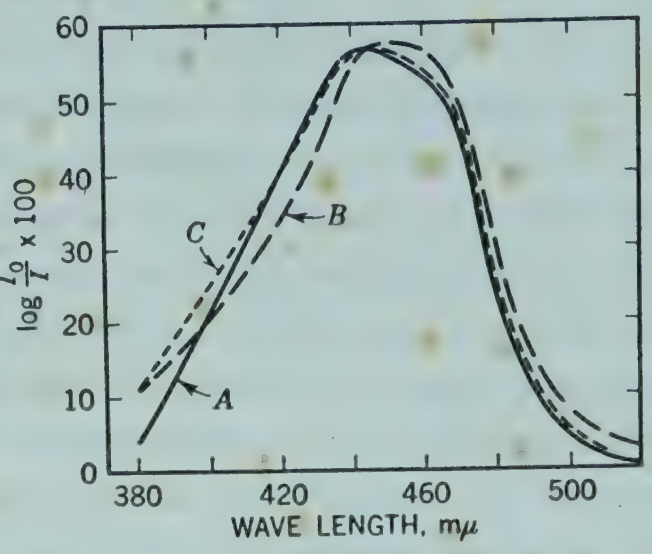


Fig. 73. Absorption curves of aniline reaction products of (*A*) pure gossypol in alcohol–ether mixture, (*B*) gossypol extracted from cottonseed meal with an alcohol–ether mixture, and (*C*) gossypol extracted from cottonseed meats with an alcohol–ether mixture (in each case absorption read against respective untreated solution).[37]

coefficient of dianilinogossypol formed under corresponding conditions from pure gossypol.

Smith reported that values for the gossypol content of cottonseed meal obtained by the spectrophotometric method corresponded to those obtained with the gravimetric method[138, 139] in most cases, but were generally higher than values obtained by the method of Lyman, Holland, and Hale.[28]

No criteria are available for establishing the specificity of the spectrophotometric method for the determination of gossypol as dianilinogossypol. Lyman, Holland, and Hale[28] reported that aromatic hydroxyaldehydes yielded reaction products with aniline exhibiting absorption spectra similar to that of dianilinogossypol. Consequently, they suggested that, if other substances besides gossypol in cottonseed meal yield colored reaction products with aniline, they must be closely related to gossypol. Smith[37] attributed the displacement of the absorption band of the aniline reaction product obtained with extracts of cooked cottonseed meal to slight modifications in the structure of gossypol extracted from cottonseed meal.

A third spectrophotometric method [127] for the determination of gossypol in extracts of cottonseed and cottonseed meal is based on the formation of a stable red product by reaction of gossypol with antimony trichloride in chloroform. The absorption spectrum of the gossypol–antimony trichloride reaction product exhibits two broad absorption bands in the near ultraviolet and visible wave length regions,[140] which can be mathematically characterized in terms of the ratios of the extinction coefficients at the maxima and the intervening minimum. For routine analysis, only the height of the band at 520 mμ need be determined. The reaction of gossypol with antimony trichloride is more rapid than that of the other components of seed and meal extracts, so that, if the absorption of the reaction product is determined within a period of ten to forty minutes after the reactants are mixed, the value of the extinction coefficient at 520 mμ serves as a measure of the concentration of gossypol in the extract. The gossypol content is calculated from the specific extinction coefficient at 520 mμ of the reaction product of antimony trichloride with pure gossypol.

Addition of a drop of acetic anhydride usually prevents the appearance of haze due to moisture in the reaction mixture. However, in the case of very wet seed or meal, it is frequently necessary to prepare more concentrated extracts than are required for the spectrophotometric analysis, in order that the concentration of water can be reduced by dilution with dry solvent before the addition of antimony trichloride.

The specificity of the antimony trichloride reaction for gossypol in extracts of cottonseed and cottonseed meal has been established on the basis of values of the ratios of the extinction coefficients at the maxima and minimum, using values obtained by reading the absorption ten minutes after mixing the reactants. When it is found that the antimony trichloride reaction cannot be applied directly to the crude extract, as may be the case with many chloroform extracts of cooked cottonseed meal and petroleum naphtha extracts of uncooked seed, the alkaline extraction method [95] is first applied for the separation of gossypol from interfering components in the crude extract.

Titrimetric Method for Estimation. Podol'skaia [135] has published a method for the determination of gossypol in ethereal extracts of cottonseed and cottonseed meal which is based on the reduction of the cupric ion in Fehling's solution. The amount of cuprous ion formed is determined by titration of the cuprous oxide precipitate with a standard solution of potassium permanganate. Podol'skaia determined the quantities of gossypol corresponding to different weights of copper reduced.

The titration method and the aniline–pyridine method of Royce and Kibler [137] yielded similar results when applied to the determination of

[140] The absorption spectrum of the reaction product of antimony trichloride with pure gossypol is shown in Figure 43, page 252.

gossypol in extracts of uncooked cottonseed. Lower values obtained by application of the gravimetric method to extracts of cooked cottonseed meal were attributed to incomplete precipitation of dianilinogossypol. It was suggested that different forms of gossypol, not precipitable by aniline, were responsible for the higher values obtained when the titration method was applied to cottonseed oil.

Because of the many reducing substances which are present in raw and cooked cottonseed, the titration method is probably not highly specific for gossypol when applied to these products.

(b) Gossyfulvin. Gossyfulvin can be completely extracted from ground or flaked cottonseed and cottonseed meal by equilibration with chloroform or diethyl ether at 3.3° C. over a period of twenty-four hours.[95, 127] Gossyfulvin appears to suffer no detectable decomposition in extracts stored at the afore-mentioned temperature for as long as forty-eight hours.

Estimation. Gossyfulvin exhibits a broad absorption band in the visible wave length region which has served as a basis for determining the purity of mixtures containing relatively high concentrations of this pigment.[32, 34] However, the concentration of gossyfulvin in extracts of cottonseed and cottonseed meal is usually quite low, and the absorption of gossypol interferes with that of gossyfulvin. No method has been found for the quantitative removal of interfering pigments from extracts containing small amounts of gossyfulvin; and none of the colored reaction products of gossyfulvin so far investigated appears to be sufficiently stable to serve as a reliable basis for a quantitative determination.

A differential method has been developed, however, which permits the determination of the approximate concentration of gossyfulvin in extracts containing preponderant amounts of gossypol. This method is based on the following properties of gossyfulvin. Upon treatment of chloroform solutions of gossyfulvin with strong mineral acids, it is rapidly converted into gossypol to the extent of 86.8% of its weight. The reaction product of gossyfulvin with antimony trichloride exhibits very little absorption at 520 mμ. Consequently, the difference in the extinction coefficients at 520 mμ of the antimony trichloride reaction product of a chloroform extract of cottonseed, before and after preliminary treatment with a strong mineral acid, serves as a measure of the amount of gossyfulvin in the extract.

Since the concentration of gossypol in the extracts is usually appreciably greater than that of gossyfulvin, the change occurring upon treatment with acid is usually quite small, and the accuracy of the method is correspondingly poor. Moreover, many cottonseed meals appear to contain pigments which, after treatment of the extract with acid, interfere with

the absorption spectrum of the antimony trichloride reaction product of gossypol.

(c) Gossypurpurin. Gossypurpurin is extracted from ground or flaked cottonseed and cottonseed meal by equilibration with chloroform at 3.3° C. over a period of twenty-four hours. In order to avoid decomposition of the pigment, the extract must be protected from light, and both the chloroform and the extraction apparatus must be free of acid or base. In extracts of cottonseed or cottonseed meal, gossypurpurin is usually stable for forty-eight hours when stored at the afore-mentioned temperature in the absence of light or in such light as is transmitted by low-actinic glass.

In the estimation of gossypurpurin by the spectrophotometric method, the specific extinction at 565–566 mμ of chloroform extracts of cottonseed or cottonseed meal is determined, and the concentration of gossypurpurin in the extract is calculated by reference to the specific extinction coefficient of pure gossypurpurin at this wave length.[95] Since the absorption band of gossypurpurin in the above-mentioned region is rather broad, reasonably accurate measurement of its height can be obtained by reading the absorption at 570 mμ with a spectrophotometer which selects bands as wide as 10 mμ.

The degree of purity of the best preparation of gossypurpurin obtained up to the present [95] has not yet been established, hence values calculated on the basis of its specific extinction coefficient do not necessarily represent the exact concentration of gossypurpurin. However, these values provide a basis for accurate comparisons of the concentrations of gossypurpurin in different samples of seed and meal.

(d) Yellow and Orange-Yellow Pigments of Immature Cottonseed. No detailed method has been published for the extraction and quantitative estimation of the yellow and orange-yellow pigments which Podol'skaia [106, 118] has detected in immature cottonseed. Podol'skaia reported [106] that these pigments are extracted from cottonseed kernels by contact with ethanol or chloroform for several hours. Their concentrations in the extracts were estimated on the basis of the heights of their characteristics absorption bands. The yellow pigment was reported [106] to exhibit two bands, at 430 to 440 mμ and at 480 to 500 mμ; and the orange-yellow pigment two bands, at 430 to 440 mμ and at 460 to 475 mμ.

2. Estimation of Extraglandular Pigments

(a) Carotenoid Pigment. Podol'skaia [111] has described the following method for the quantitative estimation of the carotenoid pigment which she found in cottonseed oil.[110] Weighed samples of finely ground seed are extracted with petroleum naphtha in a Soxhlet apparatus until

the extract is no longer colored. The method usually requires continuous extraction for eighteen to twenty-four hours, after which the solvent is evaporated, and the residual oil is treated as described below. The method of estimation is based on the stability of the carotenoids to alcoholic alkali, and the instability of the gossypol pigments upon treatment with this reagent.

A quantity of oil is treated with twice its weight of 16% alcoholic potassium hydroxide, and the mixture is heated with stirring for fifteen minutes at 50° C. The reaction is complete when the mixture becomes homogeneous. After this treatment, the solution is transferred to a separatory funnel, water is added in the amount of 125–150 ml. per 25 g. of oil, and the carotenoid pigment is extracted with petroleum naphtha (b.p. 40–60°).

The carotenoids in the petroleum naphtha extract are determined with a Duboscq colorimeter against a standard carotene or $K_2Cr_2O_7$ solution for comparison. Under these conditions, two absorption bands are observed: at 450 to 460 mμ, and at 470 to 485 mμ.

Podol'skaia reported that any gossypol which may be present in the oil does not interfere with the determination because it is largely decomposed by the alkali treatment, and residual decomposition products remain in solution in the aqueous ethanol from which the carotenoids are extracted by the petroleum naphtha.

Determination of the specific extinction coefficients at the wave lengths of maximum absorption would appear to be desirable for greater accuracy in the final estimation of the concentration of the carotenoid pigment in the petroleum naphtha extract.

(b) Oil-Soluble Yellow Pigment. No method has yet been developed for the accurate estimation of the nonacidic yellow pigment which is present in solutions of the oil of the extraglandular tissue of cottonseed.[39] The pigment is readily extracted from flaked or ground cottonseed with petroleum naphtha. Any gossypol which is also extracted from ruptured glands is subsequently removed from the petroleum naphtha extract by treatment with aqueous alkali. However, if the gossypol content of the extract is considerable, some of the other yellow pigment is also removed by this treatment.[38, 39]

The relative concentration of the yellow pigment in a given extract can be estimated on the basis of the height of the absorption band at 368 to 374 mμ, but this band is rather low and is located in the region of relatively intense absorption by other pigments of the cottonseed. Consequently, spectrophotometric measurements of petroleum naphtha extracts of cottonseed, even after extraction with aqueous alkali, do not yield very accurate measures of the concentration of the yellow pigment.

C. Development of Pigments during Growth of the Seed

1. Gossypol

Pigment glands start forming in the fifteen-day old embryo coincidentally with the differentiation of other tissue, and by the sixteenth day they are fully developed structurally.[12, 120] The first signs of gossypol are detected in the glands within a few days of their formation.[12, 120] As shown in Table 74, the formation of oil precedes that of gossypol by several days.[106, 141, 142] The delayed appearance of gossypol during the period of initiation of synthetic processes in the seed has been explained [42] on the

TABLE 74

Time of First Appearance of Gossypol and Oil in Developing Cottonseed

Age after flowering, days	Gossypol content (dry weight), %[a]	Oil content (dry weight), %[b]
16[c]	None	1.00
24[c]	None	3.12
32[c]	0.230	22.35
21[d]	0.052	8.26
25[e]	0.25	21.47

[a] Determined by precipitation of dianilinogossypol.
[b] Calculated on basis of weight of ethereal extract.
[c] W. D. Gallup, *J. Agr. Research*, **36**, 471–480 (1928).
[d] C. Caskey, Jr., and W. D. Gallup, *J. Agr. Research*, **42**, 671–673 (1931).
[e] M. Z. Podol'skaia, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov*, **1939**, 61–72.

TABLE 75

Increase in Gossypol and Oil Content during Development of Cottonseed

Values reported by Caskey and Gallup[a]			Values reported by Podol'skaia[b]		
Age after flowering, days	Gossypol content, (dry weight), %	Oil content (dry weight), %	Age after flowering, days	Gossypol content (dry weight), %	Oil content (dry weight), %
21	0.052	8.26	25	0.25	21.47
24	0.113	11.73	30	0.61	29.86
27	0.168	16.66	35	0.89	33.93
30	0.266	20.55	40	0.93	35.03
34	0.347	20.25	45	0.96	35.40
37	0.360	20.80	50	1.06	37.00
44	0.399	20.20	55	1.08	37.70
50	0.408	20.90			

[a] *G. hirsutum*, Oklahoma Triumph; from C. Caskey and W. D. Gallup, *J. Agr. Research*, **42**, 671–673 (1931).
[b] *G. hirsutum*, Variety 114; from M. Z. Podol'skaia, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov*, **1939**, 61–72.

141 W. D. Gallup, *J. Agr. Research*, **36**, 471–480 (1928).
142 C. Caskey, Jr., and W. D. Gallup, *J. Agr. Research*, **42**, 671–673 (1931).

hypothesis that this unstable polyphenolic compound cannot form until it has been furnished with the protection of the resistant gland walls. It has been suggested [15, 105, 106] that the first pigments detected in the newly formed pigment glands are precursors of gossypol.

Immediately following the appearance of oil and gossypol, the synthetic processes in the seed are intensified. Both gossypol and oil are formed at an accelerated rate (Table 75) from about the twenty-first to the thirty-fifth day after flowering, but gossypol increases at a greater rate than the oil.[106, 142, 143] After about the thirty-fifth day, the oil content of the seed remains approximately constant, but gossypol continues to increase until about the fiftieth day, when the seed are fully matured and the boll opens.[106, 142, 143]

2. Other Pigments

(a) Intraglandular Pigments. Podol'skaia [106, 118] observed that the glands of immature cottonseed remain yellow until the boll opens; their color then changes through a deeper yellow, to orange-yellow, and finally to red after the seed has been stored for varying periods of time. It was suggested that these color changes represented transformations of different forms of gossypol in the glands of the developing seed. The yellow and orange-yellow pigments appeared to represent precursors of the usual lemon-yellow form of gossypol, whereas the red pigment appeared to be the form of gossypol finally developed in the pigment glands of the fully matured and stored seed.[144]

These color transformations were reported [106, 118] to occur in all of the seed investigated, but the rate of transformation was not the same in all varieties. Red pigment glands were noted at an earlier stage in the development of Egyptian seed (Pima) than in American varieties (*G. hirsutum,* varieties 915, 8517, and 114).

TABLE 76

Variation in Carotenoid Content[a] with Development of Seed[b]

Age after flowering, days	Carotenoid content, mg./100 g.
25	0.219
30	0.131
60	0.110
80	0.096

[a] All determinations were carried out with Variety 114, *G. hirsutum.*
[b] M. Z. Podol'skaia, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1939,** 61–72.

[143] W. D. Gallup, *J. Agr. Research,* **34,** 987–992 (1937).
[144] The substance referred to by Podol'skaia as red gossypol has been shown to be composed of a mixture of gossypol and gossypurpurin. See C. H. Boatner, *Oil & Soap,* **21,** 10–15 (1944), and pages 266–267 in this chapter.

(b) Carotenoid Pigment of Cottonseed. Podol'skaia [110, 111] determined the concentration of carotenoid pigment in Variety 114 of *G. hirsutum* at different stages of development of the seed. As shown in Table 76, the content of this pigment decreased to about one-half of its original value during development and maturation of the seed.

D. Pigment Content of Mature Cottonseed

1. Influence of Environmental Factors

Investigations concerning the influence of growth conditions on the pigmentation of cottonseed have been limited to gossypol.

Schwartze and Alsberg [129] reported the first quantitative determination of the gossypol content of a large number of samples of cottonseed of widely scattered origin. The seed samples were collected from oil mills in all of the cotton-growing sections of the United States. Schwartze and Alsberg concluded that, if genetic factors influenced the gossypol content of the seed, these factors were completely masked by environmental factors. The gossypol content of individual samples of seed of widely scattered locations of growth varied by as much as 300%, and that of seed of the same variety grown in the same location varied as much as 200% from one year to the next. A general correlation was observed between gossypol and oil content and location of growth of the seed: seed from the Southwest were of low oil and gossypol content; seed from the Southeast, of intermediate oil and gossypol content; and seed grown in the Pacific coast region were highest in both oil and gossypol.

Schwartze and Alsberg noted a direct relationship between the oil and gossypol content of the seed they investigated.[145] More recently, the direct correlation between the concentrations of oil and gossypol in mature cottonseed has been confirmed by Gallup [146] and Smirnova.[15] Gallup noted, however, that the relationship is quite variable, the ratio of oil to gossypol ranging from 55:1 to 35:1 in different samples of seed.

Gallup [146] determined the gossypol and oil contents of seed of the same variety, Oklahoma Triumph 44, harvested from plants grown during successive seasons on experimental plots in several adjacent counties. The effect of different kinds of fertilizer was also investigated. Portions of his data are shown in Table 77. Approximately parallel variations in oil and gossypol contents were noted. Gallup concluded that the gossypol and oil contents of cottonseed are determined principally by the locality in which the plants were grown, and are influenced only slightly by an additional supply of plant nutrients. Weather records indicated very slight differences in mean temperature at the different locations. It was

[145] For a thorough discussion of the conclusions of Schwartze and Alsberg concerning the relation between oil and gossypol content, see Chapter IV, page 140.

[146] W. D. Gallup, *Oil & Soap,* **13,** 191–194 (1936).

concluded that the relatively high gossypol and oil contents of seed from plants grown in Bryan County the first year and in McIntosh County for two consecutive years could be attributed to the higher rainfall which occurred during the growing season in these counties.

The addition of nitrogen, phosphorus, or nitrogen and phosphorus fertilizers appeared to decrease the amounts of gossypol and oil in the seed. The gossypol and oil contents were increased in seed from plants supplied with a complete fertilizer including all three nutrient elements. Wadleigh [147] also noted that the accumulation of both oil and gossypol in the seed was favored by depletion of nitrogen reserves.

TABLE 77

Relation of Fertilizing Treatment and Locality of Growth to the Gossypol Content[a] of Cottonseed[b]

Locality	Fertilizer addition				Unfertilized	
	N	P	N and P	N, P, and K		
First year:						
Greer County	0.552	0.515	0.571	0.638	0.592	0.531
Payne County	—	0.524	—	0.578	0.560	0.538
Bryan County	0.503	0.538	0.577	0.626	0.642	0.611
McIntosh County	0.756	0.728	0.744	0.738	0.762	0.735
Second year:						
Greer County	—	0.690	—	0.714	0.658	0.685
Payne County	0.512	—	0.530	0.533	0.583	0.564
Bryan County	0.465	0.441	0.442	0.478	0.438	0.437
McIntosh County	0.687	0.714	0.638	0.777	0.708	0.707

[a] Figures represent per cent gossypol based on dry weight of delinted seed.
[b] W. D. Gallup, *Oil & Soap*, **13**, 191–194 (1936).

Smirnova [15] investigated the gossypol, oil, and protein contents of several varieties of cottonseed grown during the same year in two widely separated localities (Tashkent and Kara Kala), and during two successive years in the same locality (Tashkent). She found that the gossypol content of a given variety varied considerably in different localities and in different seasons (Table 78). No data were given on the climatic factors which might account for these differences in composition. Smirnova noted a direct relationship between the oil and gossypol contents of the seed and an inverse relationship between the oil and protein contents.

In order to determine the effect of climatic variations within the same growing season, Gallup [146] compared the oil and gossypol contents of seed from early- and late-blooming bolls. As shown in Table 79, no significant difference in the gossypol content of such seed was revealed. The gossypol

[147] C. H. Wadleigh, *Arkansas Agr. Expt. Sta. Bull.*, **368**, 49–50 (1940).

content of seed from poorly developed plants was somewhat less than that from normal plants, whereas the oil content did not appear to be affected. Wadleigh,[147] on the other hand, reported a positive correlation between the development of gossypol and oil, and the ordinal rank of flowering.

TABLE 78

Variation in Gossypol Content of Different Kinds of Cottonseed with Location and Year of Growth[a]

Species of *Gossypium*	Variety	Gossypol content[b]		
		Tashkent, 1933	Tashkent, 1934	Kara Kala, 1934
hirsutum	1306	0.50	0.63	0.57
hirsutum	169	0.57	0.71	0.62
hirsutum	182	0.80	0.72	0.89
hirsutum	$36–M_2$	—	—	0.92
hirsutum	Navrotskii	1.03	0.80	0.77
hirsutum	20042	0.99	0.83	0.83
hirsutum	13714	0.94	0.69	0.74
hirsutum	8427	1.30	—	1.25
barbadense	0670	1.09	—	1.08
barbadense	0671	1.02	—	1.34
barbadense	4666	1.32	—	1.17
—	13638	0.65	0.67	—

[a] M. I. Smirnova, *Bull. Applied Botany Genetics Plant Breeding U.S.S.R.*, **Ser. III,** No. 15, 227–240 (1936).
[b] Per cent of dry weight of the seed.

TABLE 79

Gossypol and Oil Contents of Cottonseed[a] from Early- and Late-Developing Bolls and from Bolls of Poorly Developed Plants[b]

Source of seeds	First year		Second year		Third year	
	Gossypol, %	Oil, %	Gossypol, %	Oil, %	Gossypol, %	Oil, %
Early-developed bolls	0.632	24.30	0.518	23.86	0.443	23.89
Late-developed bolls	0.542	23.69	0.508	23.88	0.498	22.69
Bolls of poorly developed plants	0.535	24.27	0.458	23.60	0.407	23.12

[a] Percentages are based on dry weight of delinted seed.
[b] W. D. Gallup, *Oil & Soap,* **13,** 191–194 (1936).

2. Influence of Genetic Factors

In order to determine the relation of chemical composition to variety, Smirnova[15] analyzed seed from a large number of varieties of plants grown in experimental plantings at Gandzha (Table 80) in the Azerbaijan

TABLE 80

Protein, Oil, and Gossypol Contents of Different Varieties of Cottonseed Grown in 1933 in Gandzha[a]

Species and variety	Time of ripening, days	Composition, %[b]			
		Water	Protein	Oil	Gossypol
G. hirsutum					
915	134	7.07	—	40.30	1.25
114	146	5.48	32.50	40.24	0.93
0246	148	6.98	32.00	41.92	1.39
0700	149	6.30	32.43	42.43	1.03
0278	151	6.84	33.81	40.81	0.77
Navrotskii	157	5.49	33.06	41.45	1.28
0491	154	4.07	—	42.60	0.91
0259	160	7.33	33.81	41.71	1.10
G. barbadense					
Fuadi	155	8.01	33.50	39.19	1.53
Ashmouni 486	161	6.59	32.93	39.71	1.47
Sakel 494	169	4.10	—	42.68	1.28
Melabessa 924	168	6.77	30.12	43.14	1.01
G. herbaceum					
Kuldzhinsk Gusa 101	124	7.19	32.68	38.24	0.47
Red Gusa 2270	140	7.92	37.87	34.88	0.15

[a] M. I. Smirnova, *Bull. Applied Botany Genetics Plant Breeding U.S.S.R.*, **Ser. III**, No. 15, 227–240 (1936) (English summary, p. 240). [b] On basis of dry weight of seed.

TABLE 81

Protein, Oil, and Gossypol Contents of Different Varieties of Cottonseed Grown in 1933 in Tashkent[a]

Species and variety	Time of ripening, days	Composition, %[b]			
		Water	Protein	Oil	Gossypol
G. hirsutum					
13791	122	5.64	30.62	42.59	0.91
13714	123	6.64	31.87	41.53	0.94
14848	123	5.72	30.94	44.54	1.31
14958	123	5.59	32.18	40.90	1.07
13656	116	7.84	33.24	38.39	0.65
1306	126	5.48	30.75	40.17	0.50
20042	133	5.37	35.87	39.37	0.99
2017–32	129	5.04	33.43	42.02	0.86
182	126	5.99	—	39.23	0.80
169	128	5.98	30.37	40.06	0.57
508	142	6.09	33.12	41.43	1.04
Navrotskii	139	4.16	35.94	37.84	1.03
8582	138	4.00	38.43	36.38	0.80
36–M_2	141	5.76	36.75	40.14	0.95
8427	142	5.18	—	41.47	1.30
G. barbadense					
0671	165	3.97	35.12	38.71	1.02
0670	162	3.81	35.43	40.23	1.09
Maarad	171	5.59	33.68	40.29	1.59
23	162	3.68	34.12	40.78	1.29
4666	164	5.38	34.25	41.69	1.32

[a] M. I. Smirnova, *Bull. Applied Botany Genetics Plant Breeding U.S.S.R.*, **Ser. III**, No. 15, 227–240 (1936) (English summary, p. 240). [b] On basis of dry weight of seed.

Republic (Transcaucasian), and from plants grown the same year (Table 81) at Tashkent in the Uzbec Republic (Midasiatic). Analysis of these data (Table 82) led Smirnova to the conclusion that genetic

TABLE 82

Interspecies and Intraspecies Variation of Protein, Oil, and Gossypol Contents of Cottonseed[a]

Species of *Gossypium*	Location and year of harvest	Composition, %[b]		
		Protein	Oil	Gossypol
hirsutum	Tashkent, 1933	30.37–39.43	36.38–43.88	0.51–1.10
barbadense	Tashkent, 1933	33.68–35.43	38.71–41.62	1.02–1.59
hirsutum	Gandzha, 1933	32.00–33.81	40.24–42.43	0.77–1.39
barbadense	Gandzha, 1933	30.12–33.50	39.19–43.14	1.01–1.53
herbaceum	Gandzha, 1933	32.68–37.87	34.88–38.24	0.15–0.47

[a] M. I. Smirnova, *Bull. Applied Botany Genetics Plant Breeding U.S.S.R.*, **Ser. III,** No. 15, 227–240 (1936) (English summary, p. 240).
[b] On basis of dry weight of seed.

factors exert a significant influence on the gossypol content of cottonseed independently of environmental factors: varieties of *G. herbaceum* being the lowest in gossypol; those of *G. hirsutum* being intermediate; and those of *G. barbadense* the highest.

Goldovskii [105] also concluded that the wide variation of gossypol content noted in different samples of cottonseed must be due to more than climatic or nutritional factors.

Smirnova [15] noted a direct correlation between the number of pigment glands and the gossypol content of individual seed. She suggested that the number of pigment glands might be the factor determining the amount of gossypol in different varieties. As shown in Table 83, the average num-

TABLE 83

Relation between Average Number of Pigment Glands and Gossypol and Oil Contents of Cottonseed[a, b]

Species of *Gossypium*	Variety	Number of glands in each seed	Gossypol, %[c]	Oil, %[c]
herbaceum	101	14	0.29	36.95
hirsutum	182	27	0.89	38.73
hirsutum	36-M_2	34	0.92	37.9
barbadense	0670	37	1.01	43.7
barbadense	0671	46	1.27	44.3

[a] M. I. Smirnova, *Bull. Applied Botany Genetics Plant Breeding U.S.S.R.*, **Ser. III,** No. 15, 227–240 (1936) (English summary, p. 240).
[b] Seed from plants grown in same place during the same season.
[c] Based on dry weight of seed.

ber of pigment glands in seed of *G. herbaceum* (of low gossypol content) is from one-third to one-half that in seed of *G. barbadense*—the latter contains three to four times as much gossypol. In both gossypol content and number of glands, seed of *G. hirsutum* are intermediate between seed of *G. herbaceum* and *G. barbadense*.[148]

3. Content of Pigments Other Than Gossypol

Podol'skaia [110, 111] noted that the carotenoid content of mature cottonseed depended upon the variety of the seed. She reported the values shown in Table 84.

TABLE 84

Relation of Carotenoid Content to Variety of Cottonseed[a]

Variety[b]	Year of harvest	Carotenoid content, %
114 (American)	1936	0.096
Navrotskii (American)	1934	0.093
8517 (American)	1934	0.077
Pima (Egyptian)	1934	0.114
Fuadi (Egyptian)	1936	0.193

[a] M. Z. Podol'skaia, *Masloboino Zhirovoe Delo*, **13**, No. 6, 8–9 (1937); *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov*, **1939**, 61–72.

[b] Varieties 114 and Fuadi were of Transcaucasian, and the others of Midasiatic growth.

Podol'skaia [106, 108] also found that the concentration of the yellow and orange-yellow intraglandular pigments, and of gossypurpurin was higher in mature seeds of Egyptian varieties than in American varieties.

E. Variation of Pigments during Storage of Cottonseed

1. Storage of Mature Cottonseed

(a) Variation under Conditions of Moderate Temperature and Humidity. Since prime oils can be obtained from normal or prime seed after prolonged storage under conditions of moderate temperature and humidity, the question of the variation of the pigments of cottonseed under these conditions has received scant attention. Nevertheless, the investigations of Podol'skaia [106, 110, 111, 118] have shown that cottonseed pigments undergo constant alteration upon storage of the seed.

Podol'skaia [106] investigated the variation in gossypol content during

[148] See Table 78, p. 312, for more data published by Smirnova, and Table 72, page 295, for variation in gossypol content of pigment glands separated from different seed. If Smirnova's conclusions are correct concerning the number of pigment glands characteristic of a given variety, growth, and storage conditions, they might account for the smaller variation in the gossypol content of the glands, which would be reflected as smaller variations in the gossypol content of the seed.

storage of seed of Variety 114 of *G. hirsutum*, and reported the results shown in Table 85. Since the gossypol content of seed of different varieties,

TABLE 85

Changes in Gossypol Content during Storage of Cottonseed (*G. Hirsutum*, Variety 114)[a]

Time of test	Moisture, %	Gossypol (dry basis), %
October	5.87	1.15
November	5.74	1.06
December	5.65	1.04
January	6.47	0.75

[a] M. Z. Podol'skaia, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov*, **1939**, 61–72.

grown under different conditions, has been shown to vary between wide limits,[15, 105, 129] it appears probable that it would also follow different patterns of alteration during storage of different kinds of seed. However, no systematic investigation has been reported of the relation between the original gossypol content of mature cottonseed, and its variation during storage of the seed.

Polol'skaia [106, 118] noted a correlation between the content of the yellow and orange-yellow intraglandular pigments, of gossypurpurin, and the water-dispersible red-purple pigment of mature cottonseed, and the development of these pigments during storage of cottonseed. The concentration of these pigments in mature seed of Egyptian varieties was found to be higher than in seed of American varieties; and upon storage of the seed the pigments increased more rapidly in the Egyptian than in the American varieties.

Incidental to their investigations of the effect of moisture on the storage properties of cottonseed, Kyame and Altschul [149] observed a definite pattern of variation of the pigments of petroleum naphtha-extracted oils of three varieties of *G. hirsutum*. The investigations were carried out with samples of Delfos 3506, Coker's 200, and Oklahoma Triumph, each grown in a different locality and subsequently stored under similar conditions for a period of about one year. The oils were extracted periodically from the stored seed and were dissolved in carbon tetrachloride for determination of their absorption spectra. Deductions concerning changes in concentrations of gossypol and gossypurpurin in the seed were based on relative extinction coefficients at 360 and 560 mμ, respectively, of these solutions. The pigment variation was found to follow approximately the same pattern in all three varieties; in the case of some of the seed a slight initial decrease in absorption at 370 and at 560 mμ

[149] J. Kyame and A. M. Altschul, *Plant Physiol.*, **21**, 550–561 (1946).

was noted, but thereafter the absorption slowly increased throughout the remainder of the storage period. As these workers pointed out, petroleum naphtha does not affect the pigment glands, hence it does not usually extract significant amounts of the intraglandular pigments. Consequently, if the absorption at 560 mμ is due to gossypurpurin, as suggested by the authors, this pigment must have been extracted from the pigment glands which were mechanically ruptured during preliminary grinding of the seed. The absorption at 360 mμ may have been due to gossypol extracted from mechanically ruptured glands, as well as to the oil-soluble extra-glandular pigment,[39] solutions of which exhibit an absorption band at 368 to 374 mμ.

(b) Variation during Storage of Moist Cottonseed. Because of their economic importance, the storage properties of moist cottonseed have been investigated over a period of many years. These properties are discussed in detail in Chapters V and XIII.

Barrow [150] reported that seed containing more than 10% moisture generate heat during storage, with attendant formation of free fatty acids in the oil and darkening of the meal. Malowan [151] found that the color of the oil obtained from field-damaged seed, *i.e.*, seed damaged by excessive rainfall before opening of the bolls but subsequently dried before harvesting, is normal. On the other hand, seed damaged by storage at high moisture levels develop excessive amounts of free fatty acids and produce dark colored oil.

Altschul and co-workers [149, 152–156] have reported a series of investigations on the effect of high moisture on the behavior of cottonseed during storage, and methods for the control of deteriorative changes during storage of such seed. During the course of these investigations it was observed [153] that oil extracted with petroleum naphtha from moist seed and stored in small sealed containers was less deeply colored than the oil extracted from the corresponding seed stored in large tanks. The color of the hydraulic-pressed oil obtained from the latter seed was even darker. It was concluded that the darker color of the oil from seed stored in large quantity was attributable to oxidation of the pigments of the seed by exposure to the action of air.

Kyame and Altschul [149] have reported that the pattern of change in the absorption spectra of oils extracted by petroleum naphtha from moist

[150] E. H. R. Barrow, *Ind. Eng. Chem.*, **7,** 709–712 (1915).
[151] J. Malowan, *Oil & Fat Ind.*, **4,** 127–130 (1927).
[152] M. L. Karon and A. M. Altschul, *Plant Physiol.*, **19,** 310–325 (1944).
[153] A. M. Altschul, M. L. Karon, L. Kyame, and M. Caravella, *Oil & Soap,* **20,** 258–262 (1943).
[154] A. M. Altschul, *Oil Mill Gazetteer,* **49,** No. 1, 8, 9, 11, 13 (1944).
[155] A. M. Altschul, M. E. Curet, M. L. Karon, C. M. Hall, and B. A. Smith, *Oil Mill Gazetteer,* **50,** No. 2, 9–13, 23 (1946).
[156] A. M. Altschul, M. L. Karon, L. Kyame, and C. M. Hall, *Plant Physiol.*, **21,** 573–587 (1946).

stored seed differs from that observed in oils extracted from stored seed of normal moisture content. The series of curves shown in Figure 74 exemplifies one type of change which occurs in the visible absorption spectra of oils extracted from moist seed stored over a prolonged period. These investigators attributed the absorption at 360 mμ to gossypol and that at 560 mμ to gossypurpurin.

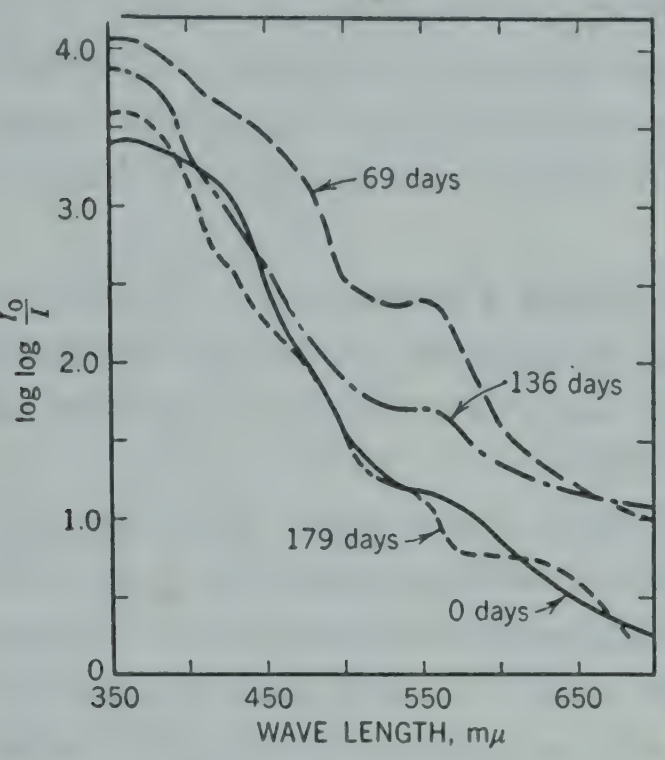


Fig. 74. Absorption spectra of oils extracted with petroleum naphtha from seed stored at high moisture content for the number of days indicated.[149]

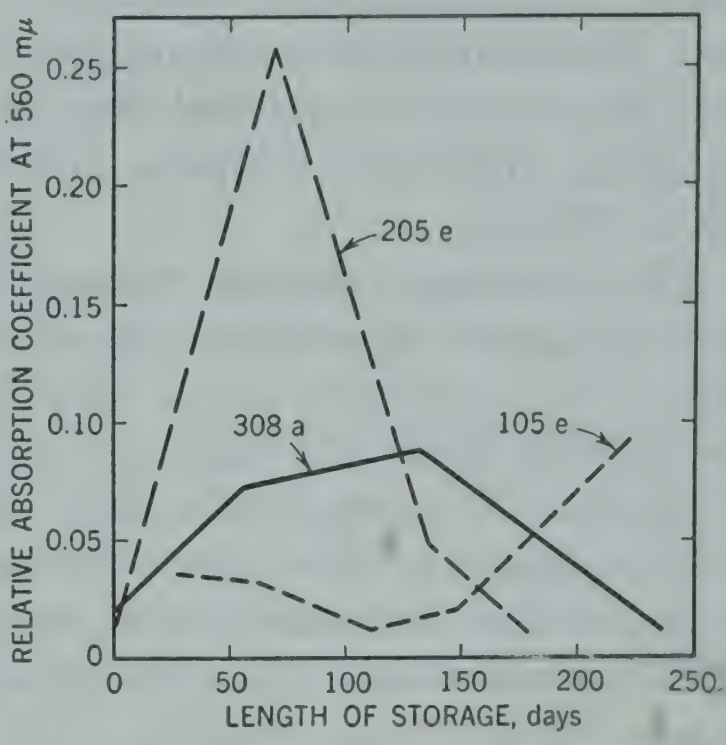


Fig. 75. Variation in relative absorption coefficients at 560 mμ of extracted oils during storage of moist cottonseed for days indicated.[149]

As shown in Figure 75, the oils extracted from two samples of moist seed, Coker's 200 (205 e) and Oklahoma Triumph (308 a), exhibited similar patterns of variation in the absorption at 560 mμ. The absorption increased to a maximum during the initial periods of storage, and then decreased upon more prolonged storage. Similar patterns of change were observed in the absorption of the extracted oils at 360 mμ. The variation in the relative absorption at 560 and 360 mμ of the oil obtained from a third series of seed, Delfos 3506 (105 e), was the reverse of that observed with the other two samples of seed; the relative absorption first decreased to a minimum and then increased during more prolonged storage.

Kyame and Altschul [149] noted similar variations in the rate of lipolysis of the same samples of moist seed during storage; the rate of lipolysis of the 200 and 300 series increased and then decreased during storage, whereas that of the 100 series decreased to a minimum and then increased. Karon and Altschul [157] had previously observed similar changes in respiratory rates during storage of the same samples of seed.

Goldovskii [105] reported that all of the gossypol of seed which have

[157] M. L. Karon and A. M. Altschul, *Plant Physiol.*, **21**, 506–521 (1946)

deteriorated through storage is "bound," *i.e.*, it is not extracted from the glands by either diethyl ether or ethanol. The pigment glands of such seed are not affected by contact with water, and the gland contents do not yield the red color reaction with concentrated sulfuric acid which is characteristic of gossypol.

The difference in the color of the oils obtained from prime cottonseed and from seed damaged by storage at high moisture levels has been interpreted [42] on the basis of the sensitivity of the pigment glands to moisture and the unstable nature of the intraglandular pigments. It has been suggested that the intraglandular pigments undergo relatively little alteration during storage of dry seed because of the protection furnished by the gland wall. During storage of moist seed the water-sensitive gland wall furnishes inadequate protection for the polyphenolic intraglandular pigments from the oxidizing action of the reactive components of the seed tissue. Thus, the polyphenolic pigments are believed to be partially converted into more deeply colored quinoid compounds. It has been further pointed out that the observed acceleration of respiration during storage of moist seed furnishes presumptive evidence of the participation of the polyphenolic intraglandular pigments in the respiration of the seed.

For a discussion of the effect of various chemical treatments on the color of stored moist cottonseed, the reader is referred to Chapter V.

2. Storage of Immature Seed

Seed obtained from immature bolls which have been prematurely broken open by frost are designated as *bollie* seed, and the oils derived therefrom as *bollie* oil.

Fash [4] observed that, whereas fresh bollie oils have a normal refined color, storage of crude bollie oil produces dark colors in the refined oil after storage for periods as short as one week. He also observed that when crude bollie oil was mixed with crude normal oil it caused rapid deterioration in the color quality of the normal oil. According to Meloy,[3] seed from plants defoliated through infestation by leaf worm or through drought or frost are of low oil content, and the oil is highly pigmented. Mixing of this oil with prime oil was reported to cause instability in the color of the prime oil.

The absorption spectra of oils extracted from immature seed have been reported by Altschul and co-workers [156] to follow a pattern of variation during storage of the seed different from that observed in the oils extracted from normal seeds. The relative absorption at 360 and 560 mμ of the extracted oil increases during storage of the immature seed, whereas it decreases during storage of mature seed.

Treatment of mature stored seed with ammonia was reported [156] to merely accelerate the rate at which the absorption of the extracted oils

decreased. The change in relative absorptions at 360 and 560 mμ of oils extracted from ammonia-treated immature seed follows an entirely different pattern of variation. The absorption at 360 mμ decreases as the period of storage is increased, whereas the absorption at 560 mμ is initially high and remains practically constant throughout prolonged periods of storage.

IV. Variation of Pigments during Processing of Cottonseed

A. Factors Determining the Nature and Distribution of Pigments in Cottonseed Products

The unique pigment system of the cottonseed kernel gives rise to many technical problems which are not encountered in the processing of other oilseeds. The pigment content of cottonseed is unusually high and variable. Most of the cottonseed pigments are complex polyphenols, which are among the most unstable of organic compounds and are readily converted to deeply colored degradation products. The properties of the pigment glands peculiar to cottonseed—in which most of the cottonseed pigments are segregated—constitute an important factor in determining the pigmentation of the products obtained by processing the seed. Most of these properties have already been reviewed in some detail, but they will be briefly summarized here insofar as they affect the pigmentation of the oil and meal obtained by different methods of processing cottonseed.

1. Chemical Instability of the Cottonseed Pigments

Gossypol, the principal pigment of cottonseed, occurs in concentrations as high as 2% of the weight of the kernel. The gossypol content of different samples of cottonseed may vary many-fold, and is dependent upon a number of factors, including species, variety, location and year of growth, maturity, and length and condition of storage. Other pigments are usually present in lesser amounts than gossypol, but the variation of most of them is of approximately the same order, and appears to be dependent upon as many factors as that of gossypol. The final pigmentation of cottonseed products is as variable as that of the original unprocessed cottonseed.

Most of the complex polyphenolic cottonseed pigments readily undergo alteration. After its isolation from other seed components, gossypol is so very unstable that simple derivatives can be prepared only by observance of the most extreme precautions. The other related pigments of cottonseed, gossypurpurin and gossyfulvin, are even more unstable than gossypol. It is doubtful whether any of these polyphenolic pigments could exist in the seed without the protection furnished by the pigment gland wall. The intraglandular pigments undergo alteration within the seed even during

storage of normal seed at moderate temperatures and in the absence of excessive amounts of moisture. The pigments of immature and of moist cottonseed vary even more widely during storage of the seed. These pigments undergo profound alteration under the extreme conditions applied in processing of cottonseed.

2. Properties of the Pigment Glands

As mentioned previously, most of the pigments of the kernel are segregated in distinct morphological structures known as pigment glands. The pigment glands possess a thick, strong, and resistant surrounding wall which, presumably, protects the gland contents from direct contact with the components of the surrounding tissue in the intact seed. These glands possess such high mechanical strength that, in seed of normal moisture content, only a small fraction are ruptured under the tremendous pressures and shearing stresses to which they are subjected during rolling or grinding of the seed preparatory to processing. The gland walls are resistant to the action of most liquids except water and a few water-miscible organic liquids of low molecular weight. Contact with water produces immediate rupture of the pigment gland, and the sensitivity of the glands to moisture is so great that they are affected by the merest traces of moisture. The effect of moisture on the glands increases at elevated temperatures. Because of the extreme instability of the intraglandular pigments, the behavior of the pigment gland wall during processing is an important factor in determining the pigmentation of the products.

3. Variations Due to Processing

The alteration of the pigments and their ultimate distribution between the oil and meal is determined by the original pigmentation of the seed and the conditions of moisture content and temperature during processing. When the seed are subjected to little heat during processing—as in the practice of the Skipin or flotation methods, or in the solvent extraction of uncooked seed—the pigments of the products are essentially those of the original seed. Their distribution between the oil and meal is determined by the condition of the gland walls and the relative solubilities of the pigments.

Oil obtained by the Skipin method (page 340) contains the carotenoid and other oil-soluble extraglandular pigments, as well as nearly all of the gossypol of the seed. Gossypol is liberated from the glands upon introduction of the large amounts of moisture employed in this process for the separation of oil. Gossypurpurin and the other pigments of cottonseed which are insoluble in cottonseed oil remain with the meal.

If moisture is rigorously excluded during processing, cottonseed oil obtained by the flotation process (page 357) contains principally the oil-

soluble extraglandular pigments and practically none of the intraglandular pigments of cottonseed. The meal is essentially free of pigments.

When anhydrous solvents, other than water-miscible organic liquids of low molecular weight, are employed for solvent extraction of uncooked cottonseed, only the soluble extraglandular pigments are extracted with the oil. The intraglandular pigments in the intact pigment glands remain with the meal. Solvents, such as methanol, ethanol, dioxane, or acetone, or aqueous mixtures thereof, rupture the pigment glands and extract most of the intraglandular pigments with the oil. When moisture is not rigorously excluded during processing, extraction with water-immiscible solvents may result in slow rupture of the pigment glands and subsequent partial extraction of the intraglandular pigments with the oil.

The pigmentation of oil and meal obtained by processing of cottonseed by the hydraulic and continuous screw-press methods, as well as by solvent extraction of cooked cottonseed, is determined by the conditions of cooking. When seed are treated with large amounts of moisture prior to cooking, the pigments of the ruptured glands are subjected to the action of heat while they are in solution in cottonseed oil and in contact with the active components of the extraglandular tissue. When seed containing relatively small amounts of moisture are heated or moisture is introduced after the seed have been heated for some time, the intraglandular pigments are subjected to the action of heat while within the relatively inert surroundings of the pigment glands. Consequently, the final pigmentation of cooked seed may vary widely, and is largely determined by the moisture content of the seed during heating. Since most of the pigment glands are finally ruptured during the customary prolonged cooking of the seed, the final distribution of the pigments of cooked seed between the expressed or solvent-extracted oils and the residual meal is determined by their solubilities in cottonseed oil, or in the oil–solvent mixture used for separating the oil from the meal.

B. Cooking of Cottonseed

1. Bound Gossypol

The theory of "bound gossypol" is based on the observation by Withers and Carruth [158] that improvement in the nutritional value of cottonseed meal produced by cooking of the seed is accompanied by a corresponding decrease in the amount of gossypol which can be extracted from the cooked seed or meal by diethyl ether. These investigators attributed the improved nutritional value of the cooked seed and of commercial cottonseed meals to their lower content of ether-extractable gossypol.

Carruth [47] found that the gossypol of cooked seed and commercial

[158] W. A. Withers and F. E. Carruth, *J. Agr. Research,* **5,** 261–288 (1915).

meal can be extracted by treatment with warm aniline. He noted that the amount of gossypol which can be extracted with ether decreases as the amount extractable with aniline increases, and as the period of cooking is prolonged. The gossypol of cooked seed was designated *D-gossypol.* It was found to constitute as much as 1% of the weight of some samples of meal. Upon extending these investigations to a large number of samples of commercial cottonseed meal, Sherwood [159] found that their content of D-gossypol varied from 0.335 to 1.076%, and was very much larger than their content of gossypol extractable with diethyl ether, which varied from 0.007 to 0.150%.

The compound formed upon treatment of cooked cottonseed with aniline was first reported [47] to be identical with dianilinogossypol. Upon further investigation, Carruth [8] concluded that the two compounds differed in elementary composition, but Clark [36] later demonstrated that the compound formed by treatment of cooked cottonseed with warm aniline is identical with dianilinogossypol. Clark renamed the compound formed by gossypol during cooking of cottonseed, *bound gossypol.*

Upon the basis of these observations, the theory of "bound gossypol" was proposed.[8, 36, 84, 158] According to this theory, gossypol combines under the influence of heat with either the free amino or free carboxyl groups of cottonseed protein. The compound thus formed is postulated to be of about the same chemical stability and physiological inertness as dianilinogossypol. Gossypol can be completely recovered from its combination with protein only by treatment of the cooked seed with warm aniline or alcoholic alkali.

Since most of the free amino groups of cottonseed protein are, presumably, aliphatic in nature, their reaction with gossypol might be expected to yield an extremely unstable and readily hydrolyzed compound similar to diaminogossypol or gossyfulvin. Likewise, if the reaction of the free carboxyl groups of the protein were like that involved in the reaction of aliphatic acids with gossypol, bound gossypol would be thermally unstable and easily hydrolyzed. Esterification of the phenolic groups of gossypol by the free carboxyl groups of the protein might explain the chemical stability and physiological inertness of bound gossypol. However, no experimental data have been presented which demonstrate the existence of bound gossypol as a chemical entity, or yield any information concerning its chemical nature.

As the result of an extensive series of investigations, Halverson and Smith [130–132, 138] concluded that the amount of gossypol which can be extracted from cottonseed meal with diethyl ether is a function of the amount of moisture in the meal and the ether, and of the temperature at which the extraction is carried out. Under conditions of high moisture

[159] F. W. Sherwood, *J. Agr. Research,* **32,** 793–800 (1923).

content and elevated temperatures, it was found [130, 131] that gossypol is continuously extracted from cottonseed meal for periods as long as seventy-two hours, and it was concluded that more prolonged treatment would result in the extraction of additional gossypol. These observations have been confirmed by other investigators.[28, 160]

Much of the difference between diethyl ether and warm aniline in their effect on cottonseed can be attributed to the behavior of the pigment gland wall. A small fraction of the gossypol of normal uncooked seed has been reported [160] to resist extraction by diethyl ether, but to react with aniline. Goldovskii [105] has reported that the pigment glands of immature seed are not affected by diethyl ether, but are readily ruptured by contact with warm aniline. Podol'skaia [106, 118] noted that the intraglandular pigments of immature cottonseed differ from gossypol with respect to their absorption spectra in the visible wave length region, but that they react with aniline to form compounds identical with dianilinogossypol. The pigment glands of seed which have deteriorated through storage have been reported [105] to be largely resistant to the action of diethyl ether, but to rupture readily upon contact with warm aniline. It was also observed [105] that the intact pigment glands of cooked cottonseed are attacked only upon treatment with aniline, and much of the material contained therein reacts with aniline to form a compound identical with dianilinogossypol.

Gossypol is readily adsorbed by active adsorbents. Thus, if cottonseed is defatted with solvents, such as the solvent naphthas, which do not attack the pigment glands and the pigment glands are subsequently ruptured, it has been found [38, 39] that most of the gossypol from the ruptured glands is adsorbed on the protein of the defatted seed. The adsorbed gossypol is not affected by diethyl ether, but it is readily eluted by acetone, dioxane, methanol, ethanol, isopropanol, or aqueous solutions of these solvents, and, presumably, by warm aniline.

During his investigations of the factors determining the nutritional value of cooked cottonseed, Gallup [161] found that the bound gossypol of cooked seed does not account for all of the gossypol of the original seed. He also noted [162] that gossypol is completely converted to bound gossypol after seed are heated without the addition of water, but that the nutritional value of the toasted seed, in contrast to wet cooked seed, is little better than that of uncooked seed containing large amounts of free gossypol. Moreover, it was found that different samples of seed cooked under different conditions but containing comparable amounts of free gossypol may produce very different physiological effects when fed to experimental animals. Gallup concluded that gossypol undergoes more complex changes

160 *Vsesoyuz. Nauch. Issledovatel Inst. Zhirov, Supplement,* **1936,** 111–115.
161 W. D. Gallup, *Ind. Eng. Chem.,* **19,** 726–728 (1927).
162 W. D. Gallup, *Ind. Eng. Chem.,* **20,** 59–63 (1928).

during cooking of cottonseed than can be accounted for by its simple conversion from free to bound gossypol, and that compounds in addition to these two affect the nutritional value of cooked cottonseed.

Several pigments of uncooked and cooked cottonseed other than gossypol react with aniline to form dianilinogossypol. The yellow and orange-yellow pigments of immature cottonseed have been reported [106, 118] to form compounds indistinguishable from dianilinogossypol. Reaction of aniline with crude hydraulic- and screw-pressed cottonseed oils containing negligible amounts of gossypol produces compounds which exhibit absorption spectra identical with that of dianilinogossypol.[95]

Thus, it would appear that the concept of bound gossypol should be redefined to include all forms of cottonseed pigments—which by reason of their solubility, their segregation within pigment gland walls of unusual resistance, or their adsorption on other seed tissue—are not readily extracted by diethyl ether, but are extracted from the seed by warm aniline and react with this compound to form dianilinogossypol. Since this includes a relatively large variety of cottonseed pigments, efforts should be made to distinguish the individual members of the group.

2. Pigment Changes during Cooking of Cottonseed

(a) Effect of Moisture. Gallup [161] investigated the effect of heat on the gossypol content of dry and moistened seed (Table 86). The con-

TABLE 86

Gossypol and Bound Gossypol Contents of Cooked Cottonseed[a]

Time of heating (hours: minutes)	Final moisture content, %[b]	Final gossypol content, %[b]	Final bound gossypol content, %[b]
Ground Cottonseed Heated Dry at 110°C.			
00:10	2.40	0.137	0.135
00:15	1.97	0.021	0.309
00:20	1.65	0.021	0.222
00:30	1.15	—	0.243
1:00	0.42	—	0.237
2:00	0.11	—	0.217
4:00	—	—	0.185
8:00	—	—	0.174
16:00	—	—	0.112
Whole Cottonseed Soaked 4 Hours and Autoclaved at 20 lb. Pressure			
00:10	43.70	0.082	0.091
00:30	44.24	0.058	0.075
1:00	46.85	—	0.048
2:00	48.01	—	—

[a] Adapted from W. D. Gallup, *Ind. Eng. Chem.*, **19**, 726–728 (1927).
[b] Original seed contained 7.51% moisture, 0.275% gossypol, and no bound gossypol.

centration of ether-extractable gossypol decreased rapidly within a short period of heating, this decrease being somewhat more rapid in wet than in dry cooked seed. In both cases, the greatest decrease occurred during the first fifteen minutes of heating. Bound gossypol was destroyed very much more slowly, particularly in the dry seed, in which it could still be detected after sixteen hours of heating.

The variations in chloroform-extractable gossypol, gossypurpurin, gossyfulvin, and gossycaerulin during heating of wet and dry seed were recently reported.[95] In order to simulate the extremes of mill practice, one series of seed was heated without addition of moisture, and moisture was added to a parallel series in amounts sufficient to increase the original moisture content of the kernels from 7.6 to 41%. The variations in content of extractable pigments observed during heating of two parallel series of whole (undecorticated) seed are shown in Figure 76. As noted by Gal-

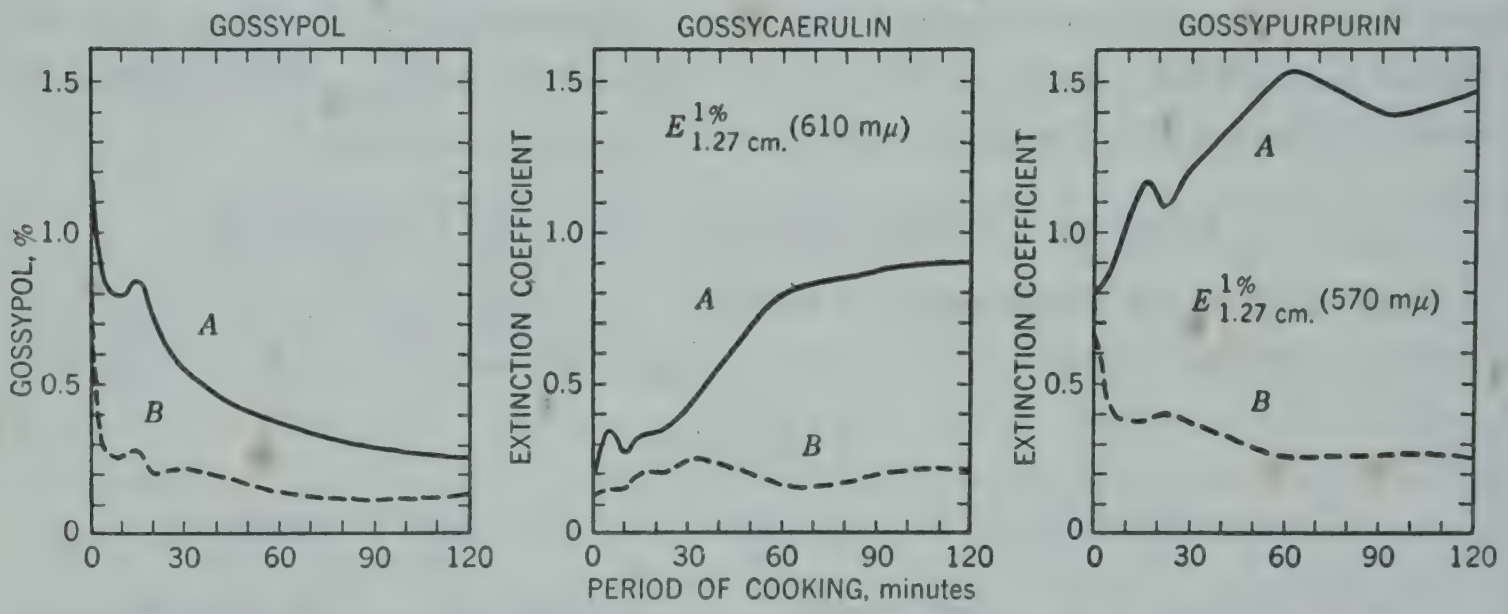


Fig. 76. Variation in extractable pigments during heating of cottonseed: *A*, dry seed; *B*, moistened seed.[95]

lup,[161] the greatest decrease in extractable gossypol occurred during the initial stages of heating, and to a greater extent in the moistened than in the dry seed. Upon continued heating, the gossypol content of the dry cooked seed approached that of the wet cooked seed.

The gossypurpurin and gossycaerulin contents of the seed cooked without addition of moisture increased as the gossypol content decreased. On the other hand, during the cooking of moistened seed the concentration of gossypurpurin slowly decreased. Gossycaerulin was formed in small amounts during the initial stages of heating moistened seed, then decreased, and subsequently increased slowly during more prolonged heating. Failure to detect gossyfulvin in the cooked seed may have been due to the thermal instability of this pigment, or to the insensitivity of the method employed for its detection. Appreciable amounts of gossyfulvin

had previously been detected [46] in several samples of hydraulic-pressed meal and oil.

Experiments to parallel the cooking of whole seed were performed [95] with whole kernels and finely ground kernels. The variations in gossypol during cooking of the wet and dry seed kernels were similar to those obtained with the whole seed. Both gossypurpurin and gossycaerulin increased somewhat less rapidly during heating of dry decorticated seed than dry whole seed. During the heating of moistened seed the contents of gossypurpurin and gossycaerulin decreased at approximately the same rate, regardless of whether whole seed, whole seed kernels, or finely ground seed kernels were heated.

A schematic representation of the conversion of gossypol into related pigments during heating of cottonseed is shown in Figure 77. It is apparent that the extent to which gossypol will be converted to a given pigment during heating of the seed will depend upon a number of factors in addition to moisture and heat. For example, gossycaerulin is formed when acidified solutions of gossypol in polar solvents are heated.[33] Similarly, as shown in Table 87, the extent of the formation of gossycaerulin during cooking of dry seed was found [33] to be roughly correlatable with the *p*H of the seed. Conversely, since gossypurpurin is formed from gossypol under slightly

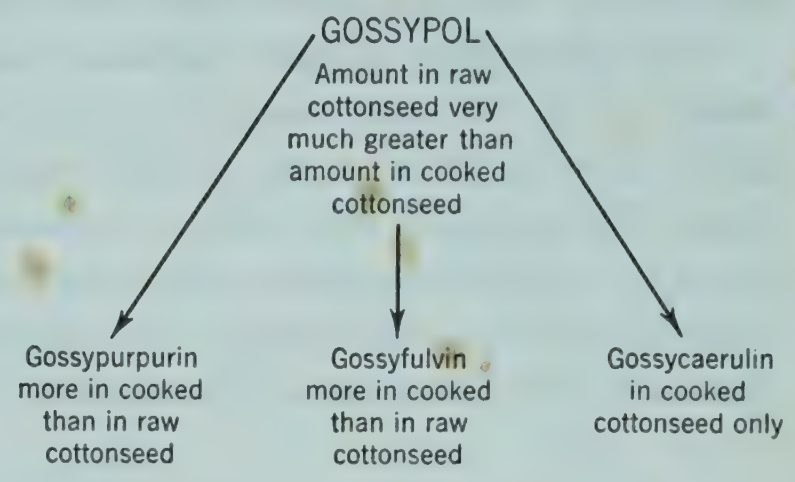


Fig. 77. Conversion of gossypol into related cottonseed pigments during cooking of cottonseed.[95]

TABLE 87

Formation of Gossycaerulin during Heating of Cottonseed[a]

Time of heating at 115° C., min.	Cooking of seed kernels			Cooking of undecorticated seed		
	Extractable gossypol, %	$E^{1\%}_{1.27\text{ cm.}}$ at 610 mμ × 100	*p*H of seed kernels	Extractable gossypol, %	$E^{1\%}_{1.27\text{ cm.}}$ at 610 mμ × 100	*p*H of seed kernel
0	0.807	1.01	6.78	1.18	1.88	6.88
5	0.64	1.66	6.85	0.835	3.46	6.58
10	0.914	1.88	6.68	0.795	2.67	6.64
15	0.939	2.57	6.62	0.844	3.33	6.62
20	0.902	2.52	6.63	0.715	3.34	6.61
30	0.906	4.48	6.89	0.552	4.22	6.60
60	0.574	4.16	6.46	0.376	8.08	6.64
90	0.458	5.97	6.40	0.294	8.79	6.35
120	0.329	6.32	6.36	0.260	9.09	6.25

[a] C. H. Boatner, C. S. Samuels, C. M. Hall, and M. C. Curet, *J. Am. Chem. Soc.*, **69**, 668–672 (1947).

alkaline conditions, the extent of its formation in cooked seed might be expected to bear an inverse relation to the *p*H of the seed. As shown in Figure 76, gossypurpurin increased during some periods of heating as gossycaerulin increased, and in other cases the relationship was reversed. It is evident, however, that additional factors affect the formation of these pigments during cooking of cottonseed. Moreover, because of the thermal instability of all of the conversion products of gossypol, they probably decompose as they are formed, and the rate of their decomposition may finally equal the rate of their formation during prolonged heating of the seed. The conditions which determine the formation of gossyfulvin during cooking of cottonseed have not been investigated.

(b) Behavior of the Pigment Glands during Cooking of Cottonseed. Speculations concerning the behavior of the intraglandular pigments during the cooking of cottonseed have yielded conflicting conclusions. Thornton [115] has stated that cooking of cottonseed was necessary in order to dehydrate the resin contents of the glands and thereby prevent them from dissolving in the expressed oils. According to Reeves and Beasley,[163] the rupture of the pigment glands during cooking and the sub-

TABLE 88

Effect on Cottonseed Pigment Glands of Dry and Wet Cooking[a]

Sample no.[b]	Time of cooking, minutes	Condition of glands	Condition of tissue
D_0	0	Intact	Normal
D_5	5	Intact	Slightly dark; yellow in spots
D_{10}	10	Few broken	Slightly dark; yellow in spots
D_{15}	15	Few broken	Yellow around glands
D_{20}	20	Some partially broken	Yellow around glands
D_{30}	30	Some broken, but still colored	Yellow around glands
D_{60}	60	Some emptied, some broken	Yellow around glands; other tissue darker than D_{30}
D_{90}	90	Many broken, some emptied completely	Red around glands; other tissue darker than D_{60}
D_{120}	120	Most emptied or broken	Dark red around glands; other tissue very dark
W_0	0	Most intact, but cloudy	Light colored; very brittle
W_{10}	10	Half intact; others broken, but still colored	Yellow around glands; very brittle
W_{20}	20	Most broken and partially emptied	Red around glands; very brittle
W_{60}	60	Some still intact, but cloudy	Red around glands; darker than W_{20}; very brittle
W_{120}	120	Most completely emptied; few intact and cloudy; others partially emptied	Red around glands; other tissue very dark and very brittle

[a] C. H. Boatner, C. M. Hall, R. T. O'Connor, and L. E. Castillon, *J. Am. Oil Chem. Soc.*, **24,** 97–106 (1947). [b] D_0–D_{120}, no water added prior to cooking; W_0–W_{120}, water added before cooking in the proportion of 100 ml. of water to 200 g. of seed.

[163] R. G. Reeves and J. O. Beasley, *Cotton and Cotton Oil Press,* **38,** No. 49, 3 (1937).

sequent spreading of their contents into the oil is probably the most important factor in causing the dark color of oils obtained from cooked seed.

During the recent investigation [95] of the pigmentation of wet and dry cooked seed, the effect of moisture was correlated with the condition of the pigment glands in the seed. Microscopic examination of seed sections revealed (Table 88) that the presence of moisture determined the rate at which the pigment glands were ruptured and their contents expelled into the surrounding tissue. In the case of the moistened seed, some of the pigment glands were ruptured even before heating, and the remainder were ruptured after heating for twenty minutes. The glands of the unmoistened seed remained largely intact until heating had been prolonged for a considerable period.

Since the moisture content determines the rate at which the pigment glands rupture during the heating of cottonseed, it determines also the environment of the intraglandular pigments while they are being subjected to elevated temperatures. Although little is known concerning the nature of the nonpigmented components of the glands or of the extraglandular tissue, it seems probable that differences in the pigmentation of wet and dry heated seed are due to the circumstance that interconversion of the pigments follows different courses when the pigments are in contact with the oil and tissue outside the glands and when they remain inside the glands during heating.

It is quite evident, however, that the changes which the very unstable pigments undergo during heating of the seed are very complex, and cannot be adequately explained on the basis of our present incomplete knowledge of the chemistry of the pigments and of the other constituents of cottonseed.

C. Processing of Cottonseed by Expression Methods

1. Preliminary Heating of the Seed

Processing of cottonseed by either the hydraulic- or continuous screw-press methods, as presently practiced in the United States, nearly always involves some preliminary heating or tempering of the seed. Since very high pressures are employed in screw pressing, the seed are usually not subjected to as much cooking as in hydraulic pressing. It has been the practice to add little or no moisture prior to heating of seed designated for screw pressing, since maximum expression of oil is obtained from seed of relatively low moisture content.[164–166]

[164] G. S. Jamieson, *Vegetable Fats and Oils,* 2nd ed., Reinhold, New York, 1943.
[165] W. R. Woolrich and E. L. Carpenter, *Mechanical Processing of Cottonseed,* Univ. Tenn. Eng. Expt. Sta., Knoxville, 1935.
[166] K. S. Markley and D. F. J. Lynch, *Proc. Cotton Research Council,* **1,** 211–224 (1940).

Cottonseed are usually subjected to rather prolonged heating for processing by the hydraulic-press method, and varying amounts of moisture are added either before or during cooking. In actual mill practice, the amount of moisture added to the seed and the duration of cooking varies widely; the conditions are usually based on experience with the type and quality of seed received at a given mill, and are also regulated so as to best fit the schedule of the press room. Maximum yield of oil is the usual criterion of optimum cooking conditions. In spite of the fact that the oil and meal are graded on the basis of color, [2, 3] control of color during processing of seed is usually of secondary consideration.

Moistening of the seed prior to heating has been recommended by some investigators; [165, 167] whereas others [168, 169] have reported that best results are obtained by the addition of moisture after the seed have been heated.

Initial moisture contents of 10 to 12% are customarily recommended.[115, 168–170] It appears to be generally agreed [168–173] that the seed should be heated at as low a temperature and for as short a period of time as required for reduction of the original moisture of the seed to the level necessary for maximum expression of the oil.

Diverse theories have been proposed concerning the function of cooking and of moisture during cooking. According to some investigators, [115, 170] moisture and heat are essential for complete rupture of the oil cells; while others [105, 163, 174] have reported that the majority of the oil-containing cells are ruptured during preliminary rolling of the seed—so that the principal function of heating is to coagulate the protein and increase the fluidity of the oil. Neuman [175] has reported that the oil-containing cells of cottonseed are so very sensitive to moisture that they are ruptured and the liberated oil is coalesced in the presence of the merest traces of moisture.

The considerable variation of color in oils produced by expression methods is well known, and the removal of color is one of the more important problems of the oil refiner. Nevertheless, very little information is available concerning the processing factors responsible for variations in the color of cottonseed oil and meal. It appears to have been established that prolonged cooking at high temperatures causes excessive fixation of

[167] H. C. Graebe, U.S. Pat. 1,707,949 (1929).
[168] T. J. Harrell and C. W. McMath, U.S. Pat. 2,064,158 (1936).
[169] M. K. Thornton, Jr. and C. R. Bailey, *Ind. Eng. Chem.*, **23,** 833–834 (1931).
[170] W. R. Woolrich and E. L. Carpenter, *Chem. & Met. Eng.*, **40,** 291–292 (1933).
[171] M. K. Thornton, Jr., *Oil & Soap,* **14,** 151–152 (1937).
[172] W. H. Baskervill, J. A. Glass, and A. H. Morgan, *Oil Mill Gazetteer,* **51,** No. 11, 56–63 (1947).
[173] A. M. Goldovskii, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1939,** 52–60 (English summary, p. 60); *Chem. Abst.*, **36,** 5663 (1942).
[174] A. M. Goldovskii, N. F. Neuman, and V. V. Solovev, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1936,** 88–97 (English summary, pp. 96–97); *Chem. Abst.*, **32,** 1128 (1938).
[175] N. F. Neuman, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1936,** 98–110 (English summary, pp. 109–110); *Chem. Abst.*, **32,** 1128 (1938).

color in both oil and meal. Addition of moisture after preliminary heating of the seed has been reported [168, 171] to lower the color of the expressed oil.

The results of several mill-scale tests,[95] during which processing conditions were considered, have yielded some information concerning the relation of conditions during cooking to the pigmentation of the oil and meal obtained by both the hydraulic- and continuous screw-press methods. The pigmentation of the meals obtained by the two methods was found to be approximately the same. However, the principal pigment of the crude, screw-pressed oil was entirely different from that of the crude, hydraulic-pressed oil, and the refined and bleached screw-pressed oils were more highly colored than the corresponding hydraulic-pressed oils.

The seed designated for screw pressing had been heated without the addition of water, whereas moisture was added before cooking the seed designated for hydraulic pressing. Since other processing conditions were approximately the same for both methods, it was concluded that the presence of moisture during cooking was the principal factor responsible for the lower pigmentation of the hydraulic-pressed oil.

During the same investigation,[95] the pigmentation of hydraulic-pressed oils and meals produced at two different mills was compared. The processing conditions were about the same at both mills, but the crude, refined, and bleached colors of the oils produced at one mill were more pronounced than from the other mill. The pigment content of the seed processed at the mill producing the more deeply colored oil was higher than that of the seed processed at the other mill. Since this appeared to be the only important difference, it was concluded that the pigmentation of the processed oil was largely determined by the original pigment content of the seed. On the basis of these conclusions, it might be expected that the addition of a larger proportion of water to highly pigmented seed prior to cooking would improve the color quality of the oil and meal obtained from this type of seed.

2. Pigments of Expressed Oils

(a) Gossypol. *Methods of Estimation.* Most of the methods which have been proposed for the estimation of gossypol in crude hydraulic- and screw-pressed cottonseed oil are based on the formation of dianilinogossypol. Dianilinogossypol precipitates very slowly in the presence of oil, but Royce and co-workers [27, 136, 137] have reported that the addition of pyridine materially accelerates precipitation. In the presence of aniline and pyridine, gossypol precipitates as dipyridyl-dianilinogossypol.[26, 27] Pyridine is removed by heating the precipitate at 160°C., and gossypol is calculated on the basis of the residual dianilinogossypol.[27] Complete precipitation of gossypol from crude oils by the use of aniline and pyridine has been reported,[27] to require seven to fourteen days.

Halverson and Smith [176] have recommended constant agitation and a temperature of 43°C. for acceleration of the precipitation of dipyridyl-dianilinogossypol. The addition of gossypol (100 mg. for 15–40 mg. of gossypol in the crude oil) was also recommended by these authors in order to accelerate precipitation. Royce, Harrison, and Deans [27] had previously reported that preliminary addition of relatively large amounts of gossypol accelerated the precipitation of dipyridyl-dianilinogossypol, but reduced the accuracy of the determination.

The titrimetric method developed by Podol'skaia,[135] which is based on the reduction of the cupric ion by gossypol, was reported to be equally applicable to the determination of gossypol in seed and meal extracts and in oils. Values obtained by the titration method were reported to be comparable with those obtained with the gravimetric method except for oils which had been subjected to unusually high temperatures, in which higher values were obtained with the titration method. These higher values were attributed to the reducing action of forms of gossypol which did not react with aniline because of their alteration under the influence of heat.

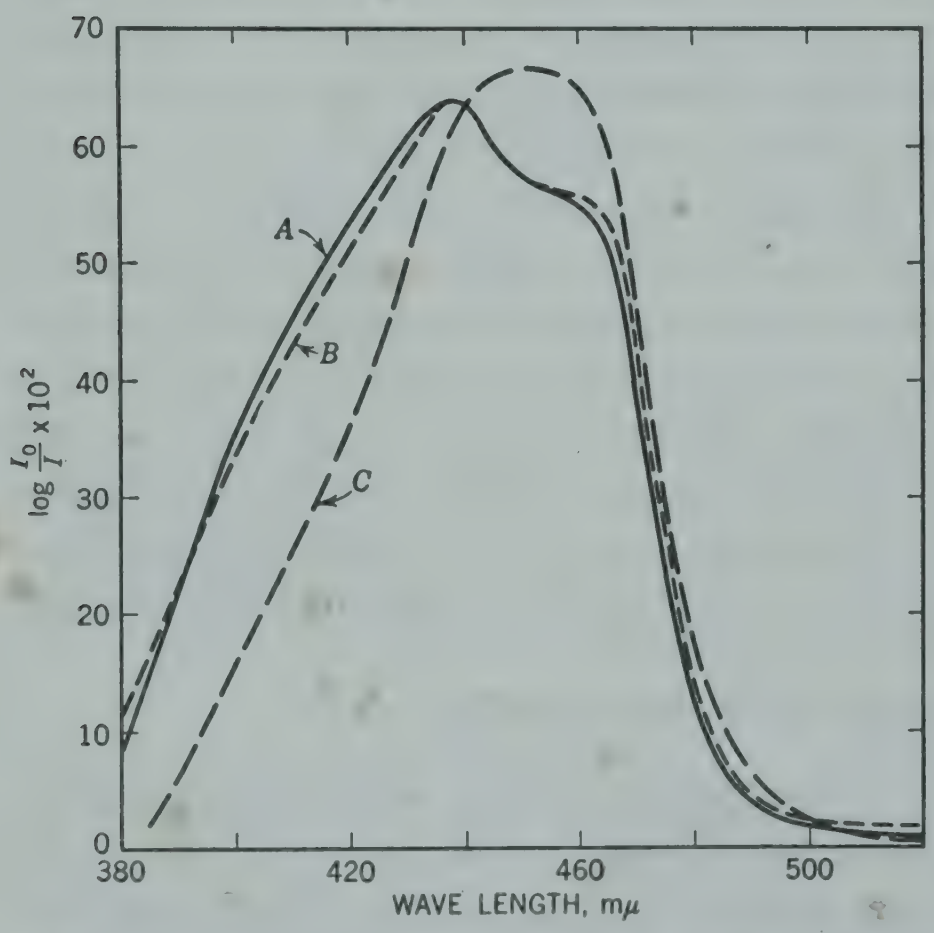


Fig. 78. Absorption spectra of aniline reaction products in Skellysolve B of (*A*) pure gossypol, (*B*) crude screw-pressed oil, and (*C*) crude hydraulic-pressed oil.[37]

The recently reported spectrophotometric method of Smith [177] is based on measurement of the characteristic absorption spectrum of dianilinogossypol. Solutions of the crude oil in commercial hexane (Skellysolve B) are heated with aniline. Typical absorption spectra of the aniline reaction products of pure gossypol, a crude hydraulic-pressed oil, and a crude screw-pressed oil as reported by Smith are shown in Figure 78. The absorption spectra of the aniline reaction products of pure gossypol and of the crude screw-pressed oil are of identical shape. The difference in the curve given by the crude hydraulic-pressed oil was attributed by Smith to a slight alteration in the structure of the gossypol

[176] J. O. Halverson and F. H. Smith, *Ind. Eng. Chem., Anal. Ed.*, **13**, 46–48 (1941).
[177] F. H. Smith, *Ind. Eng. Chem., Anal. Ed.*, **18**, 41–43 (1946).

molecule, but no experimental data were presented in support of this conclusion.

The unsuitability of direct application of the antimony trichloride spectrophotometric method to the determination of gossypol in crude cottonseed oil has been attributed [46] to the presence of preponderant amounts of interfering substances. An alkaline extraction method has recently been developed [95] for the isolation of gossypol from other pigmented components of extracts of cottonseed and meal and of crude oils. The material isolated from several samples of crude screw-pressed oils by this method did not yield antimony trichloride reaction products characteristic of gossypol. Alkaline extraction of several samples of crude hydraulic-pressed oil did not remove sufficient pigmented material to yield a visible reaction with antimony trichloride. Since the same oils had yielded aniline reaction products exhibiting absorption spectra similar to that of dianilinogossypol, it was concluded that aniline is not specific for gossypol, but reacts with pigments other than gossypol in crude expressed oils.

Gossypol Content of Crude Oils. Since crude expressed cottonseed oil served as the source of gossycaerulin [97] and of gossypol [7, 18] for early investigations of these pigments, it appears probable that the crude oils contained appreciable amounts of gossypol. The high concentration of gossypol in these oils can be attributed to the fact that the early processing of cottonseed involved very little preliminary heating of the seed. Expressed oils obtained by modern methods of processing, involving preliminary cooking of the seed, usually contain very small amounts of gossypol. Royce and co-workers [27, 136, 137] have reported that the gossypol content of crude hydraulic-pressed oils ranges from 0.039 to 0.210%, and the concentration of most frequent occurrence is about 0.05% gossypol. One sample of crude screw-pressed oil was reported [27] to contain 1.386% gossypol.

(b) Other Pigments. *Carotenoid Pigment.* The presence of xanthophylls in crude cottonseed oils has been recognized [164] for some time, but very little experimental data were published concerning the nature of this pigment or the extent of its occurrence prior to the work of Podol'skaia.[110, 111] This investigator reported [111] that the content of the pigment in crude cottonseed oil is largely determined by the amount in the original seed. As shown in Table 89, the crude oils investigated contained very slight concentrations of the carotenoid pigment. However, since very little of the pigment is removed during alkali refining, the concentration of this pigment in crude oils may be an important factor in determining the color of the refined oils. The behavior of the carotenoid pigment of cottonseed toward bleaching agents employed for cottonseed oil was not reported.

Chlorophyll. This pigment has frequently been detected [112–114, 164] in crude cottonseed oil by means of its characteristic absorption band in the visible region. Very little of the chlorophyll of crude oils is removed

during alkali refining, but it appears to be completely removed during subsequent bleaching of the oils.

Resin Pigments. Several investigators [113, 163, 164] have attributed the dark color of crude cottonseed oil to the presence of resin pigments. However, little data have been published concerning these pigments in cottonseed oil, and the failure of Tobler [117] to obtain any evidence for the existence of resins in the cottonseed kernel casts considerable doubt on the possibility of their occurrence in crude cottonseed oil.

TABLE 89

Carotenoid Content of Cottonseed Oil[a]

Processing method	Treatment of the oil	Carotenoid content, mg/100 g. oil
Solvent naphtha extraction of raw seed	Desolventized	0.392
	Desolventized	0.380
	Desolventized	0.304
	Desolventized	0.353
	Desolventized	0.456
	Desolventized	0.279
Cold pressing	None	0.225
	None	0.301
	None	0.302
	Alkali refined	0.261
	Alkali refined	0.281

[a] M. Z. Podol'skaia, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov*, **1939**, 83–94 (English summary, p. 94); *Chem. Abst.* **36**, 7064 (1942).

Hull Pigments. It has been shown [95] that hot cottonseed oil extracts negligible quantities of pigmented material from cottonseed hulls, even after prolonged steaming of the hulls. Consequently, it can be concluded that inclusion of hulls does not affect the color of oils expressed from cooked seed.

Pigments of Unidentified Nature. The relation between the pigmentation of hydraulic and screw-pressed oils was recently determined [95] by means of two series of mill-scale tests run at one mill in which seed were processed by both methods, and at a second and a third mill at which only one of the methods was employed. As shown in Table 90, the colors of the refined and bleached screw-pressed oils were found to be more intense than those of the corresponding hydraulic-pressed oils. The refined and bleach colors of the hydraulic-pressed oils (CS 166-HO and CS 166-2-HO) produced at the mill where more highly pigmented seed were processed were higher than those of the oils (CS 167-HO and CS 167-2-HO) obtained from less highly pigmented seed.

The absorption spectra (Fig. 79) of the crude hydraulic-pressed oils demonstrated the probable presence of two principal pigments, with ab-

sorption maxima at 380 to 382 mμ and 398 to 403 mμ, respectively. These pigments were present in higher concentration in the more deeply colored crude oil (CS 166-HO). Alkali refining of the oils removed the principal crude oil pigments, and revealed the presence of at least two additional

TABLE 90

Comparison of Refining Characteristics of Hydraulic- and Screw-Pressed Oils[a]

Oil[b]	FFA, %	Refining loss, %, at lye strength (Bé.), indicated				Lovibond color					
						Crude[c]		Refined		Bleached	
		12°	14°	16°	20°	Y	R	Y	R	Y	R
166–HO	0.74	4.1	4.3	—	—	70	18.3	35	5.6	20	1.0
167–HO	0.89	6.1	6.4	—	—	70	10.8	35	5.2	20	1.2
166–EO	1.0	—	—	7.6	—	—	—	35	10.3	35	4.2
166–2–HO	1.2	6.6	6.4	—	—	—	—	35	6.8	20	2.8
167–2–HO	1.0	4.0	4.0	—	—	70	22.5	35	5.7	20	1.3
166–2–EO	1.5	—	—	13.2	19.6	—	—	35	20.3	35	10.2

[a] C. H. Boatner, C. M. Hall, R. T. O'Connor, and L. E. Castillon, *J. Am. Oil Chem. Soc.*, **24**, 97–106 (1947).

[b] HO designates hydraulic, and EO, screw-pressed oils. Corresponding numbers represent oils produced at the same mill.

[c] Color of crude oils read in 1-inch cell; others in standard 5¼-inch cell.

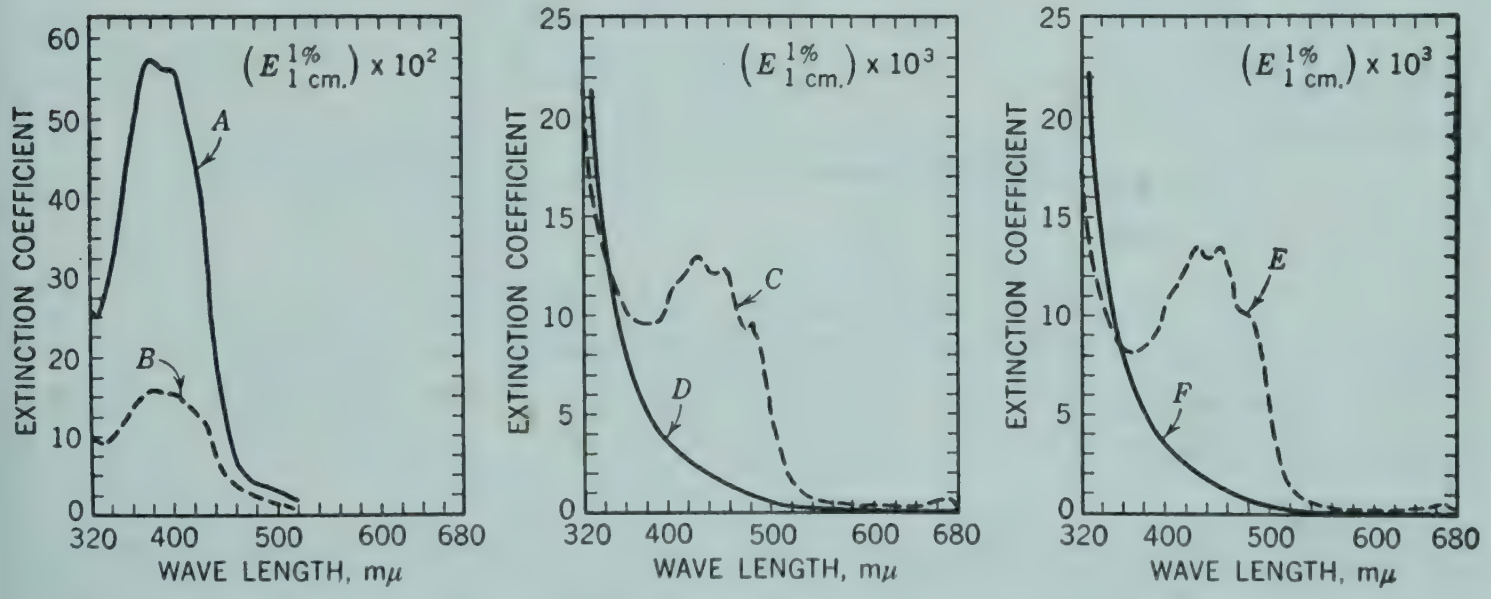


Fig. 79. Visible and near ultraviolet absorption spectra of hydraulic-pressed cottonseed oils: (*A*) CS-166-HO-crude; (*B*) CS-167-HO-crude; (*C*) CS-166-HO-refined; (*D*) CS-166-HO-bleached; (*E*) CS-167-HO-refined; (*F*) CS-167-HO-bleached.[95]

pigments, with absorption maxima at 430 to 434 mμ, 452 to 455 mμ, and 480 to 482 mμ. Most of the latter pigments were removed by bleaching, but the more deeply colored refined oil was not as readily bleached as the less deeply pigmented oil.

On the basis of these observations, it was concluded that, although the pigments of the crude hydraulic-pressed oils were different from gossypol, they behaved like gossypol with respect to their removal during alkali

refining. The crude oil containing greater quantities of the pigments with absorption maxima at 380 to 382 mμ and 398 to 403 mμ yielded an alkali-refined oil containing less of the pigments with absorption maxima at 430 to 434 mμ, 452 to 455 mμ, and 480 to 482 mμ. Consequently, it was proposed that the pigments present in the alkali-refined oils were not formed during the treatment with alkali, but were present in the crude oils, although they could not be detected until the preponderant amounts of the crude oil pigments had been removed by alkali treatment. The bleached oils exhibited no selective absorption in the visible region; but more deeply colored bleached oils were obtained from the more deeply colored refined oils.

The screw-pressed oils were more deeply colored (Table 90), and their absorption spectra (Fig. 80) differed from those of the corresponding

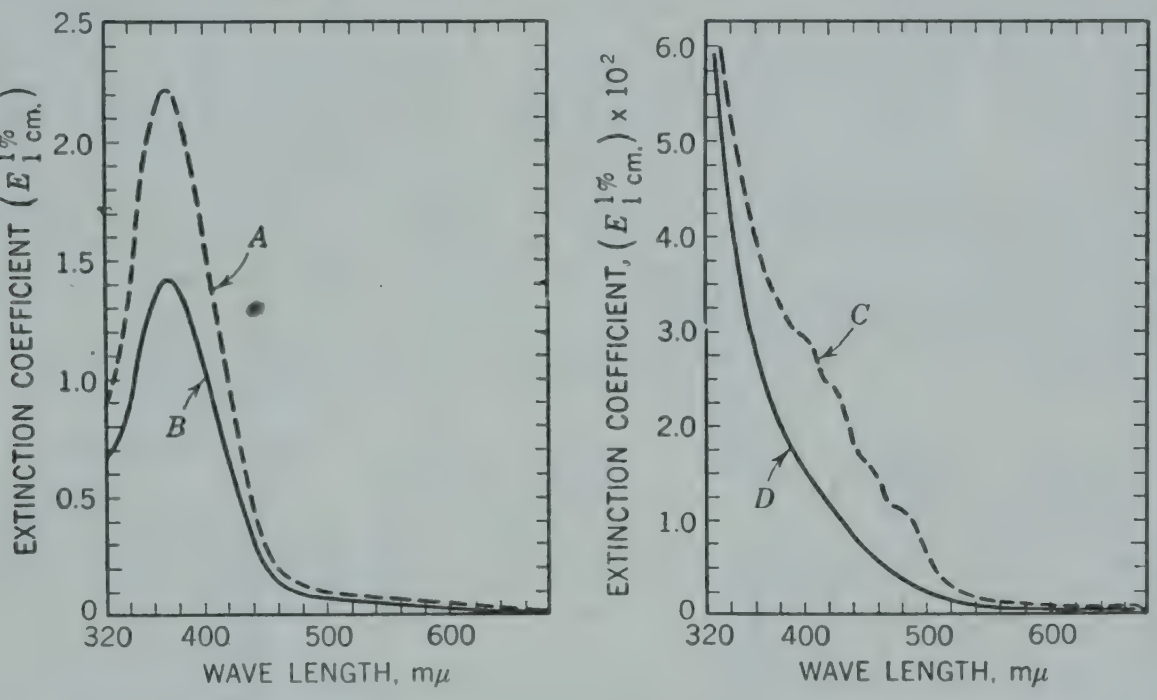


Fig. 80. Visible and near-ultraviolet absorption spectra of screw-pressed cottonseed oils: (*A*) CS-166-EO-crude; (*B*) CS-166-2-EO-crude; (*C*) CS-166-EO-refined; (*D*) CS-166-2-EO-bleached.[95]

hydraulic-pressed oils (Fig. 79). The observation of a single absorption maximum at 367 to 371 mμ indicated the probable presence of only one principal pigment in the crude screw-pressed oils, in contrast to the two pigments indicated by the absorption spectra of the crude hydraulic-pressed oils. Crude screw-pressed oils of similar absorption spectra were obtained at two independent mills employing similar processing methods. Most of the color was removed during alkali refining of the screw-pressed oils, and the absorption maximum at 367 to 371 mμ disappeared.

The alkali-refined screw-pressed oils were more deeply colored than corresponding hydraulic-pressed oils, and their absorption spectra exhibited no well-defined maxima, but only a series of inflections. Thus, the presence of a relatively large number of pigments was indicated, and it

was concluded that these pigments probably represented decomposition products of the unstable pigment present in the crude oil. The bleached oils obtained from the screw-pressed oils exhibited absorption spectra similar to those obtained from hydraulic-pressed oils, but were more highly colored.

None of the pigments of the processed oils could be identified with any of the pigments previously isolated from raw or cooked cottonseed. However, since seed containing larger amounts of gossypol and gossypurpurin yielded more highly pigmented oils, it was concluded that most of the pigments of the crude oils resulted from the decomposition of gossypol and gossypurpurin. No experimental confirmation of these conclusions was offered. No conjectures were made concerning the origin of the pigments which were detected in the alkali-refined oils.

Since hydraulic- and screw-pressed oils of very different pigmentation were obtained from the same seed, it appeared that the differences were entirely attributable to the processing conditions. Seed designated for hydraulic pressing were moistened before heating, whereas no moisture was added before cooking of the seed designated for screw pressing. No other important differences in processing conditions were observed, and laboratory-scale investigations of the changes in pigmentation during cooking of cottonseed had indicated that moisture is the most important single factor determining the nature of these changes. Consequently, it was concluded that preliminary moistening of the seed was responsible for conversion of the seed pigments to the stable and readily removed pigments of the hydraulic-pressed oils obtained from the cooked seed.

3. Pigments of the Pressed Meals

(a) Gossypol. Many of the methods for the determination of gossypol in cottonseed and cottonseed oil have been reported [27, 28, 37, 46, 47, 134, 135, 137] to be equally applicable to its determination in cottonseed meal. As previously pointed out, the specificity of most of these methods for gossypol in extracts of cottonseed meal has not been established, and is somewhat doubtful. The antimony trichloride spectrophotometric method,[46] the specificity of which is readily determined, has been found[95] to be directly applicable to the extracts of only a limited number of meals. It has not been possible to determine whether the failure to obtain a reaction characteristic of gossypol in a large number of extracts of meals to which this test has been applied is attributable to the absence of gossypol in these meals or the presence of a preponderance of other pigments.

The gossypol content of pressed cottonseed meal is usually very slight, and frequently negligible. Nevertheless, many investigators have been concerned with methods for the determination and the elimination of gossypol from cottonseed meal because of the apparent correlation of the

gossypol content with the nutritive value of cottonseed meal.[158] Different investigators have reported the following concentrations of gossypol in various samples of hydraulic- and screw-pressed meals: 0.020–0.118%,[28] 0.051–0.113%,[37] 0.179–0.235%,[46] 0.045–0.228%,[159] 0.065–0.100%,[178] and 0.055–0.252%.[179]

Withers and Carruth [158] were the first investigators to note that the gossypol content of pressed meals was reduced in proportion to the extent of cooking of the seed and the amount of moisture present during cooking. For the commercial production of cottonseed meals of low gossypol content, Sawyer [180] proposed the addition of relatively large amounts of moisture to the seed before cooking. An alternative procedure consists in moistening and recooking the meal obtained by the usual expression methods. The decrease in gossypol content of the meal obtained from seed cooked in the presence of increasing amounts of moisture has been investigated rather extensively by Sewell [179] and Lyman, Holland, and Hale.[181] The original moisture content of the seed required for elimination of all but traces of gossypol in meal obtained from the cooked seed has been usually designated as about 14.5%,[168, 181, 182] although Sewell recommends 45%.[179] Sewell concluded that the boiling point of water constitutes the critical cooking temperature for elimination of gossypol from pressed meal.

Palmer [102] attributed the yellow color of cottonseed meal to the presence of the flavone pigment, gossypetin. According to Thornton,[115] the dark color of scorched meats is the result of the decomposition of the pentosans contained in cottonseed hulls. Goldovskii, Podol'skaia, and Mirer [183] have reported that gossypol plays the principal role in determining the color of cottonseed meal. They based their conclusions on the formation of yellow, red, and brown colors in seed which had been extracted with diethyl ether and then heated in contact with solutions of gossypol in refined cottonseed oil. The color of the seed tissue was found to increase as the period or the temperature of heating was increased. Similar heating experiments conducted with aqueous solutions of raffinose demonstrated that the yellow and brown colors produced on the seed tissue were very much lighter than those produced by gossypol.

(b) Other Pigments. The absorption spectra in the visible and near ultraviolet wave length range of chloroform extracts of several sam-

[178] A. M. Goldovskii and M. Z. Podol'skaia, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1936,** 55–61 (English summary, p. 61); *Chem. Abst.,* **32,** 1127 (1938).

[179] W. E. Sewell, *Alabama Polytech. Inst. Agr. Expt. Sta. Bull.,* **259** (1943).

[180] D. F. Sawyer, U.S. Pat. 1,553,634 (1925).

[181] C. M. Lyman, B. R. Holland, and F. Hale, *Ind. Eng. Chem.,* **36,** 188–190 (1944).

[182] C. W. McMath, *Chemical, Biological and Clinical Study of Proflo,* Traders Oil Mill Co., Fort Worth, 1939.

[183] A. M. Goldovskii, M. Z. Podol'skaia, and E. A. Mirer, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1936,** 71–77 (English summary, p. 77); *Chem. Abst.,* **32,** 1127 (1938).

ples of hydraulic- and screw-pressed meals (Fig. 81) have been presented [95] as evidence that the meals contain essentially the same extractable pigments, but that these differ from the pigments of the corresponding expressed oils. Meal (CS 166-PC) obtained from more highly pigmented seed by the hydraulic-press method was found to contain more of the ex-

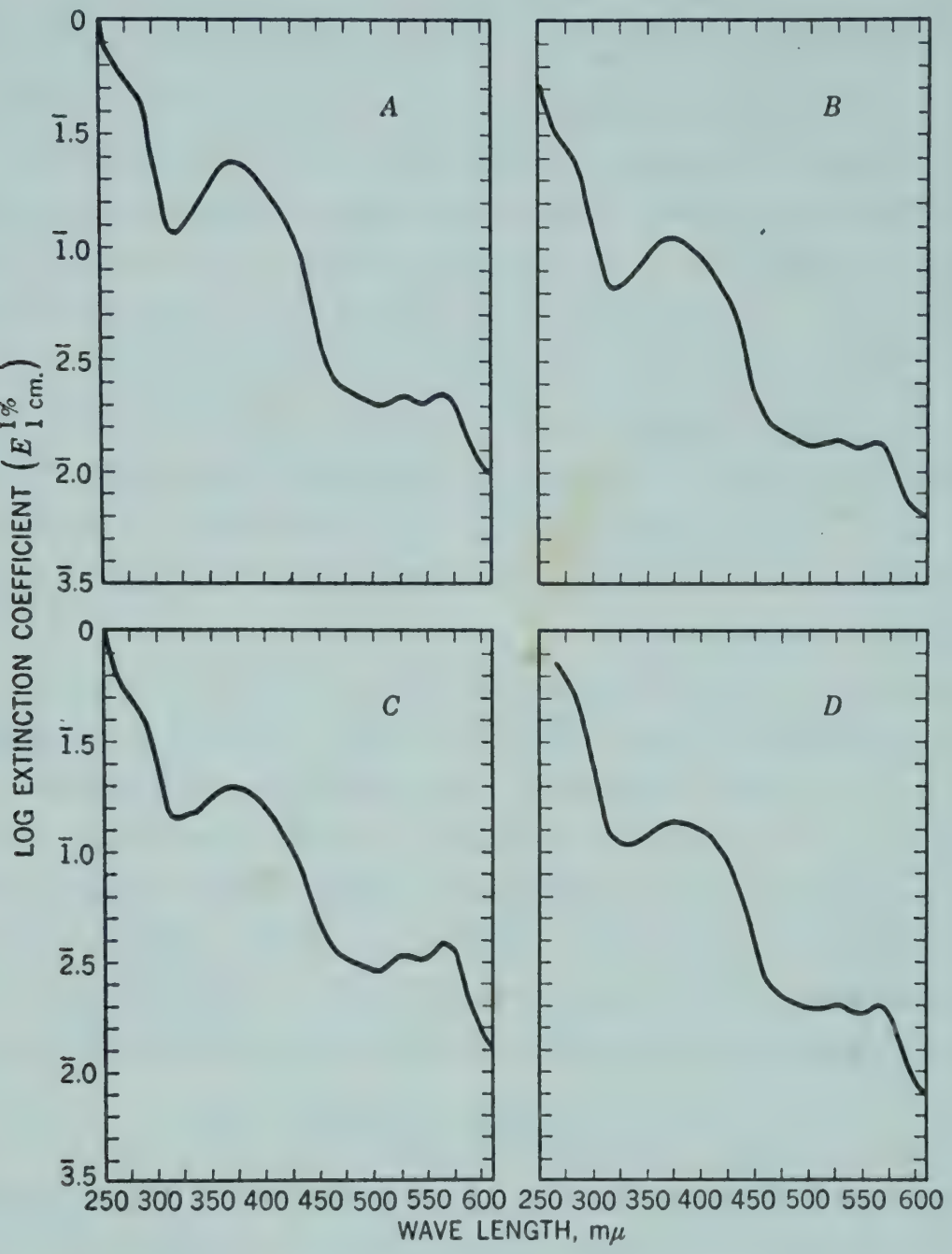


Fig. 81. Visible and near ultraviolet absorption spectra of chloroform extracts of hydraulic- and screw-pressed cottonseed meals: (*A*) CS-166-PC; (*B*) CS-167-PC; (*C*) CS-166-EC; (*D*) CS-166-2-EC.[95]

tractable pigments than meal (CS 167-PC) obtained from less pigmented seed. The pigment content of meal (CS 166-PC) obtained by hydraulic pressing was greater than that (CS 166-EC) obtained by screw pressing of the same seed.

The configuration of the absorption spectra was interpreted as indicating the presence of two principal pigments in the extracts. The absorption maxima at 526 to 530 mμ and 565 to 567 mμ, which had been shown [29, 95] to be characteristic of gossypurpurin, were attributed to the presence of this pigment in the extracts. The similarity of the absorption maximum at 368

to 374 mμ to that of gossypol was noted, but the antimony trichloride reaction product of the extract was not characteristic of gossypol. Consequently, it was concluded that the absorption maximum at 368 to 374 mμ indicated the presence in the extracts of a previously unidentified pigment. No further properties of this pigment have been reported.

D. Processing of Cottonseed by the Skipin Method

The recently developed Skipin method [105, 178, 184–186] differs from other methods for the processing of oilseeds by its fuller utilization of the action of water for releasing the oil. The first stage in the process consists in the introduction of steam for a period of about an hour until the moisture content of the seed has been raised to about 20% and the temperature is about 70° C. After thorough kneading of the moistened meal, approximately 50% of the oil, designated as forepress, forepan, prevat, or Skipin oil, rises above the meal and is readily separated. Morozov [187] has reported that the process is not applicable to the processing of seed which have been damaged by heating during storage, since the yield of oil obtained from such seed is very low.

After removal of the Skipin oil, the moisture content of the meal is reduced in heated drying vats. The meal is then reprocessed for the residual oil by the usual expression or extraction methods.

Application of the Skipin method to the processing of cottonseed results in oils and meal of very different pigmentation than those obtained by other methods. The pigment content of Skipin cottonseed oil is very different from that of the oils extracted or expressed from the Skipin meal, and the final pressed or extracted meal is dark, red-brown in color.

1. Pigmentation of Skipin Oil

Upon introduction of moisture into cottonseed for separation of the oil, the pigment glands rupture and gossypol dissolves in the oil; it is largely unaltered, because of the relatively low temperatures to which the seed are subjected. Consequently, Skipin oil contains a large proportion of the gossypol of the seed. The gossypol content of Skipin oil has been reported [185, 186, 188] to constitute 0.8 to 1.2% of the weight of the oil, in contrast to the average content of 0.05% gossypol in hydraulic-pressed oils. Skipin [185] reported the following values for one sample of

[184] A. I. Skipin, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1935,** 40; *Chem. Abst.,* **29,** 7682 (1935).

[185] A. I. Skipin, *Masloboino Zhirovoe Delo,* **12,** 379–381 (1936); *Chem. Abst.,* **31,** 1645 (1937).

[186] A. M. Goldovskii and M. Z. Podol'skaia, *Masloboino Zhirovoe Delo,* **10,** No. 7, 22–24 (1934); *Chem. Zentr.,* **II,** 4035 (1934).

[187] I. Morozov, *Masloboino Zhirovoe Delo,* **12,** 433–435 (1936); *Chem. Abst.,* **31,** 1645 (1937).

[188] A. I. Skipin and M. Ssokolova, *Masloboino Zhirovoe Delo,* **10,** 4–11 (1934); *Chem. Zentr.,* **I,** 2912–2913 (1935).

cottonseed. The original seed kernels contained 31.61% oil, and 0.53% gossypol. A yield of 39.5% of the total oil was obtained by the Skipin process, and its gossypol content was found to be 1.11%.

The content of pigments other than gossypol has not been investigated in detail, but the statement has been made [188] that Skipin oil contains most of the coloring matter of the seed. In view of the extreme insolubility of gossypurpurin in cottonseed oil, it appears unlikely that very much of this pigment would be found in Skipin oil.

Skipin and Ssokolova [188] recorded the properties of Skipin and hydraulic-pressed cottonseed oils shown in Table 91. Skipin oils have

TABLE 91

Comparison of Skipin with Hydraulic-Pressed Cottonseed Oil[a]

Type of oil	Color, Lovibond red units	Refractive index	Free fatty acid
Skipin	20–36	0.9220–0.9224	Higher[b]
Skipin, hydraulic-pressed	9–17	—	—
Hydraulic-pressed	14.5–25	0.9210–0.9238	Lower[b]

[a] A. Skipin and M. Ssokolova, *Masloboino Zhirovoe Delo*, **10**, No. 8, 4–11 (1934); *Chem. Zentr.*, **I**, 2912–2913 (1935).

[b] Reversed for storage-damaged seed.

been reported [105, 178, 188] to exhibit very much lower refining losses than hydraulic-pressed oils, and to form very compact foots, which vary from dark red to black in color. The very low refining losses of Skipin oils have been attributed to their high gossypol content. Both the color and gossypol content of the crude oils have been reported [188] to decrease upon storage of the oils, but the effect of these alterations upon the refining characteristics of the oil does not appear to have been determined.

2. Pigmentation of Oil and Meal Obtained by Reprocessing Skipin Meal

Skipin has stated [186] that nearly all of the gossypol remaining in the meal after removal of the Skipin oil is converted into bound gossypol during drying of the meal preparatory to reprocessing.

Reprocessing of the meal by the hydraulic-press method is said [105, 178, 186, 188] to yield oils of negligible gossypol content and high refining loss. Oils extracted with petroleum naphtha from the dried Skipin meal have likewise been reported [189, 190] to contain very little, if any, gossypol and to exhibit very high refining losses. By mixing the oils obtained by

[189] I. V. Gavrilenko and P. Keinov, *Masloboino Zhirovoe Delo*, **6**, No. 7–8, 7–17 (1930); *Chem. Zentr.*, **II**, 3478 (1930).

[190] I. V. Gavrilenko, *Masloboino Zhirovoe Delo*, **14**, No. 6, 5–9 (1938); *Chem. Abst.*, **33**, 5688 (1939).

reprocessing with the Skipin oil, the refining losses are comparable to those of the usual hydraulic-pressed oils.[105, 185]

The dark, red-brown color of the meal obtained after expression of the oil has been found [105, 178, 183] to detract from the value of the meal as a livestock feed, since Russian farmers associate such colors with overcooking and reduced nutritive value. Goldovskii, Podol'skaia, and Mirer[183] noted that corresponding red and brown colors were produced when cottonseed which had been extracted with diethyl ether was heated for relatively long periods in contact with solutions of gossypol in refined cottonseed oil at concentrations comparable to those observed in Skipin oils. They attributed the dark color of Skipin meal to the adsorption of decomposition products of gossypol formed during drying and reprocessing of the meal after removal of the Skipin oil. They concluded that the Skipin meal was darker than the usual pressed meals because of the higher concentrations of gossypol released into the oil during moistening of the seed for separation of the Skipin oil.

E. Solvent Extraction of Cottonseed

Although direct solvent extraction has been recommended for processing cottonseed over a period of many years,[170, 191–196] at the present writing (1946) it has not been applied on an industrial scale in the United States, and does not appear to be widely practiced in other countries. The successful application of this method for the processing of soybeans,[197] as well as current trends toward the development of continuous processes requiring a minimum of labor, has caused a revival of interest in the feasibility of economical production of marketable oil and meal by direct solvent extraction of cottonseed.

For many years, in Europe, meals obtained by hydraulic and continuous screw pressing have been reprocessed for their residual oil by solvent extraction. The oils obtained have been reported [195, 196] to be less highly pigmented than the original expressed oils. Oil extracted from cooked seed has been found [198] to be comparable to expressed oils with respect to refining loss and color.

Control of color is not the only problem which is encountered in the successful processing of cottonseed by direct solvent extraction of uncooked seed,[105,195, 196] but it is an important one. The unique pigment

[191] A. F. Sievers and J. D. McIntyre, *Cotton Oil Press,* **4,** No. 10, 44–48 (1921).
[192] J. H. Shrader, *Cotton and Cotton Oil Press,* **4,** No. 12, 42–45 (1921).
[193] D. Wesson, *Oil & Fat Ind.,* **7,** 217–218 (1930).
[194] D. Wesson, *Oil & Soap,* **10,** 151 (1933).
[195] K. S. Markley, *Oil Mill Gazetteer,* **51,** No. 3, 16–21 (1946).
[196] K. S. Markley, *Cotton and Cotton Oil Press,* **47,** No. 17, 3–6 (1946).
[197] K. S. Markley and W. H. Goss, *Soybean Chemistry and Technology,* Chemical Pub. Co., Brooklyn, 1944.
[198] H. S. Olcott, *Ind. Eng. Chem.,* **33,** 611–615 (1941).

system of the cottonseed kernel not only differentiates it from other commercial oilseeds, but is responsible for many difficulties encountered in adapting the usual solvent extraction procedures to the processing of this seed. Recent publications [16, 195, 198-200] which have reviewed the advantages and disadvantages of this process for cottonseed, as compared with the established expression methods, have been principally concerned with the difficulties involved in avoidance or removal of color in the extracted oil, and deactivation or removal of pigments in the meal.

1. Factors Determining the Distribution of Pigments between Oil and Meal

(a) Behavior of the Pigment Glands during Solvent Extraction. The earliest investigators [121-124] of the anatomy of the cottonseed noted the occurrence of the pigment glands, and reported their reaction with water. Carruth [8] later suggested the probable importance of these glands in determining the transformations of the pigments during processing of cottonseed. For a great many years the role of the pigment glands was overlooked, but it has recently been shown [38, 39, 41, 42] that the properties of the gland wall largely determine the pigmentation of solvent-extracted cottonseed oil and meal.

All of the gossypol and gossypurpurin of the kernel have been shown [39] to occur in the pigment glands. Since these are the most abundant, the most deeply colored, and the most unstable of the pigments in the kernel, most of the color observed in solvent-extracted oil and meal can be attributed to gossypol and gossypurpurin, or their decomposition products. The pigment glands have been shown to possess a rigid, thick, encircling wall which is broken only under severe mechanical stress or by contact with water and a few water-miscible organic solvents. Consequently, the intraglandular pigments will remain within the pigment glands in the meal, unless processing conditions are chosen such as to rupture the gland walls.

Since a very small fraction of the pigment glands is broken during rolling or grinding of cottonseed, unless the seed are of high moisture content, seed prepared for solvent extraction usually contain most of the pigment glands intact. The amount of ruptured pigment glands is largely determined by the conditions and solvents employed for extraction of the oil.

As shown in Table 92, prolonged exposure of finely divided seed to a series of the hydrocarbon and chlorinated hydrocarbon solvents usually employed for extraction of oil was found to result in the rupture of very few of the exposed pigment glands. The slow extraction of the intra-

[199] W. D. Harris, *Agr. Mech. Coll. Texas Bull.*, **12** (1941).
[200] A. L. Pope, *A Literature Survey of Solvent Extraction, Vegetable Oil Seeds: Cottonseeds,* Report No. 3, Blaw-Knox, Philadelphia, 1944.

TABLE 92

Effect of Organic Liquids on Pigment Glands[a]

Previous treatment	Physical state[b]	Solvent	Appearance after 24 hours' contact
Ground	P	Petroleum ether	Practically all glands intact
Ground	P	Diethyl ether	Yellow skeletons of broken glands
None	C	Hexane	Practically all glands intact
None	C	Petroleum ether	Practically all glands intact
None	C	1,1,2-Trichloroethane	Practically all glands intact
Hexane extracted	F	1,1,2-Trichloroethane	Practically all glands intact
None	C	1,1,2-Trichloroethylene	Practically all glands intact
Hexane extracted	F	1,1,2-Trichloroethylene	Practically all glands intact
None	C	1,1,2,2-Tetrachloroethane	Practically all glands intact
Hexane extracted	F	1,1,2,2-Tetrachloroethane	Practically all glands intact
None	C	1,1,2,2-Tetrachloroethylene	Practically all glands intact
Hexane extracted	F	1,1,2,2-Tetrachloroethylene	Practically all glands intact
None	C	Benzene	Practically all glands intact
Hexane extracted	F	Benzene	Practically all glands intact
None	C	Tetralin	Practically all glands intact
Hexane extracted	F	Tetralin	Practically all glands intact
None	C	Mineral oil	Practically all glands intact
Hexane extracted	F	Mineral oil	Practically all glands intact
None	C	1,4-Dioxane	Yellow skeletons of broken glands
Hexane extracted	F	1,4-Dioxane	Yellow skeletons of broken glands
None	C	Acetone	Yellow skeletons of broken glands
Hexane extracted	F	Acetone	Yellow skeletons of broken glands
None	C	Ethyl methyl ketone	Yellow skeletons of broken glands
Hexane extracted	F	Ethyl methyl ketone	Yellow skeletons of broken glands
None	C	Diethyl ether	Yellow skeletons of broken glands
Hexane extracted	F	Diethyl ether	Yellow skeletons of broken glands
None	C	Chloroform	Purple skeletons of broken glands
Hexane extracted	F	Chloroform	Purple skeletons of broken glands
None	C	Petroleum ether	Practically all glands intact
None	C	Diethyl ether	Yellow skeletons of broken glands
None	C	Chloroform	Purple skeletons of broken glands
None	F	Hexane	Practically all glands intact
None	F	Petroleum ether	Practically all glands intact
None	F	Diethyl ether	Yellow skeletons of broken glands
Hexane extracted	F	Diethyl ether	Yellow skeletons of broken glands

[a] C. H. Boatner and C. M. Hall, *Oil & Soap*, **23**, 123–128 (1946).
[b] P, powder. C, cross section. F, flakes.

glandular pigments effected by chloroform and diethyl ether was shown [42] to be the result of the normal, slight content of moisture in these solvents. When seed were treated with either of these solvents after removing as much moisture as possible from both the seed and the solvent, relatively small amounts of gossypol and gossypurpurin were extracted.

In the presence of moisture, hydrocarbons and chlorinated hydrocarbons—which normally do not affect the pigment glands—were found [38, 39] to extract appreciable amounts of the pigments. As shown by the data in Table 93, the amount of gossypol in oils extracted with petroleum naphtha

TABLE 93

Extraction of Gossypol from Cottonseed by Light Petroleum Naphtha (Skellysolve F)[a]

Preparation of seed for extraction	Treatment of solvent	Conditions of extraction		Gossypol extracted, % of total[b]
		Time	Temperature, °F.	
Ground meats wetted, then dried[c]	None	5 min.	76	58
Seed hulled and flaked[d]	None	2 hrs.	76	32
Meats flaked, dried[c]	Dried[e]	24 hrs.	38	12
Seed dried,[c] hulled, and ground	Dried[e]	24 hrs.	38	0

[a] C. H. Boatner, C. M. Hall, R. T. O'Connor, and L. E. Castillon, *Botan. Gaz.*, **109**, No. 2 (Dec., 1947).
[b] Gossypol determined on basis of antimony trichloride reaction of chloroform extracts of original seed samples and of petroleum naphtha extracts.
[c] Dried in vacuum desiccator over Drierite for 24 hours.
[d] Moisture content of flaked meats, 8.44%.
[e] Dried by treatment with calcium chloride.
[f] Moisture content of dried seed, 3.85%.

is determined not only by moisture during extraction, but also by the moisture content of the seed when they are rolled or ground preparatory for extraction. Since the mechanical strength of the pigment glands is very much reduced in the presence of moisture, cottonseed oil can be extracted entirely free of the intraglandular pigments only by desiccating the seed before they are ground or flaked.

Since complete removal of moisture from seed and solvents is impractical, most solvent-extracted cottonseed oils contain some of the intraglandular pigments. Moisture will accumulate during large-scale continuous extraction operations and produce increased rupture of the glands with consequent increase in the color of the extracted oil, unless precautions are taken for frequent or continuous removal of moisture from the system. The observation [16, 105, 198–202] that commercial grades of petroleum

[201] H. Rosenthal, U.S. Pat. 2,254,245 (1941).
[202] H. L. E. Vix, E. F. Pollard, J. J. Spadaro, and E. A. Gastrock, *Ind. Eng. Chem.*, **38**, 635–642 (1946).

naphtha and liquid hydrocarbons of low molecular weight extract very lightly pigmented oils indicates that these solvents usually contain very little moisture. But Goldovskii and Podol'skaia [203, 204] have reported that the oil extracted with petroleum naphtha (benzine) contained 10 to 15% of the gossypol of the original seed when continuous extractions were carried out on an industrial scale at 70° to 80° C. for periods as long as thirty hours. The moisture of the seed was not reported.

Increase in temperature has been found [95] to increase the tendency of the pigment glands to rupture. Thus Rosenthal's observation [201] that the color of oils extracted with liquid propane and butane at very low temperatures is very much less than that of oils extracted with the same solvents at higher temperatures may be explained in terms of the increased number of pigment glands ruptured at the higher temperature.

The observation that commercial grade chlorinated aliphatic hydrocarbons usually extract deeply colored oils under actual processing conditions [16, 198, 199] and conflicting reports [191–193] concerning the color of cottonseed oil extracted with benzene cannot be completely interpreted on the basis of the published data. The dark color of the extracted oils obtained with these solvents may have resulted from the presence of moisture or from elevated temperatures during extraction, or both.

Water-miscible alcohols, ketones, and ethers have been shown [39] to rupture the pigment gland wall. Although their action is fairly rapid, it is slower than that of water, and the rapidity with which aqueous mixtures of these solvents attack the pigment gland walls has been found (Table 71, page 291) to increase in proportion to the water content of the mixture. The pigment glands are attacked most rapidly by mixtures containing such high proportions of water that most of the pigments are expelled from the glands in suspension. Addition of more of the organic solvent accomplishes solution of the suspended pigments. Thus, rapid extraction of both the oil and pigments is most efficiently accomplished by first treating the seed with water or a dilute aqueous solution of the organic solvent, and then adding organic solvent in sufficient quantity to dissolve the pigments and oil.

As shown in Table 93, petroleum naphtha extracts only part of the pigments with the oil, even when the glands are ruptured by preliminary moistening of the seed. Solvents such as diethyl ether, chloroform, and other chlorinated hydrocarbons, in which water is somewhat soluble, can be employed for the extraction of pigments and oil by subjecting the seed to prolonged contact with the moist solvent. Processing of cottonseed with these solvents would probably prove to be impractical because of the

[203] A. M. Goldovskii and M. Z. Podol'skaia, *Masloboino Zhirovoe Delo,* **14,** No. 5, 9–12 (1938); *Chem. Abst.,* **33,** 5688 (1939).

[204] A. M. Goldovskii and M. Z. Podol'skaia, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1939,** 72–83 (English summary, p. 83).

slowness with which they accomplish complete extraction of the intraglandular pigments.

(b) Solubility of Pigments in Mixtures of Oil and Solvent. The extraglandular carotenoid pigment of cottonseed has been reported [110, 111] to be soluble in cottonseed oil, as well as both polar and nonpolar organic solvents, such as the petroleum naphthas and aqueous ethanol. Consequently, all solvent-extracted cottonseed oil will contain all of this pigment which occurs in the original seed. The other extraglandular pigments of the cottonseed kernel [39] have not been isolated, so nothing is known concerning their solubility in solvents other than cottonseed oil.

Gossypol is very soluble in cottonseed oil, but almost insoluble in aliphatic hydrocarbons. Thus, light petroleum naphtha was found (see Table 93) to extract only 58% of the gossypol from seed which had been moistened in order to rupture all of the pigment glands before treatment with the solvent. Because of the solvent action of cottonseed oil for gossypol, the ratio of solvent to seed during the initial stages of extraction will largely determine the amount of gossypol extracted by petroleum naphthas from cottonseed of a given moisture content. Very little gossypol is dissolved as the extraction progresses and the extraction mixture becomes increasingly more dilute with respect to cottonseed oil. Consequently, the pigment content of oils obtained by continuous extraction would probably differ from that of oils obtained by batch extraction.

Although gossypol is of limited solubility in diethyl ether, benzene, and chlorinated hydrocarbons, most of the gossypol from ruptured glands is dissolved in the relatively large volumes of these solvents employed for extraction of the oil.

Aqueous mixtures of water-miscible alcohols, ketones, and ethers have been found [38, 39] to dissolve all of the gossypol expelled from the glands, unless the proportion of water is very high. Eighty-five per cent aqueous ethanol has been reported [205] to extract all of the pigments with the oil, when the extraction is carried out at 78° C. Most of the oil is then precipitated, and the pigments and some of the oil are retained in the aqueous ethanol, when the extract is cooled.

Pure gossypurpurin is virtually insoluble in cottonseed oil and in most of the more common organic solvents except acetone and 1,4-dioxane, but its solubility is slightly increased in the presence of preponderant amounts of gossypol. Chlorinated hydrocarbons and diethyl ether usually dissolve all of the gossypurpurin exposed to their action by rupture of the pigment glands, whereas petroleum naphthas are usually unable to dissolve all of the relatively small amounts which are expelled from the small

[205] M. Sato, T. Inaba, and K. Kitagawa, *J. Soc. Chem. Ind. Japan, Supplement,* **30,** 50B (1938).

fraction of pigment glands ruptured during extraction with the latter solvents.

When cottonseed are treated with acetone or 1,4-dioxane, all of the gossypurpurin is extracted along with the other pigments and oil. Contrary to the report [205] that 85% aqueous ethanol extracts all of the pigments from cottonseed, it has been found [38, 39] that extraction with methanol or ethanol yielded meals containing the yellow decomposition product of gossypurpurin.

Since gossypurpurin is very unstable in all of the usual organic solvents—except chloroform at relatively low temperatures—extracted oils usually contain only the yellow decomposition product of gossypurpurin. Gossypurpurin in intact glands in the meal is relatively stable, but meals resulting from extraction of seed with solvents, such as aqueous alcohols—which are capable of rupturing all of the pigment glands but incapable of dissolving all of the released gossypurpurin—usually contain the yellow decomposition product of gossypurpurin.

(c) Pigments of the Hulls. Markley [206] has reported that the characteristic red-brown color of cottonseed hulls is largely attributable to the presence of a relatively insoluble and stable xylan compound. Cold 2% alcoholic sodium hydroxide extracts this pigment as well as the lignin of the hulls. He found the isolated pigment to be insoluble in cold absolute alcohol, diethyl ether, or acetone. Gill and Greenup [207] have reported that the red-brown pigment is also extracted with water.

The presence of hulls has been reported to have no effect on the color of oils extracted with liquid propane and butane,[201] hexane,[202] or chloroform.[38, 95] Shrader [192] attributed the dark color of the oil which he obtained by extraction with benzene to the presence of hulls. However, in view of the failure of other hydrocarbons to extract any color from hulls, it appears probable that the color of his oil was due to the extraction of pigments of the kernels.

The very small amount of gossypol extracted with aqueous ethanol from cottonseed hulls has been attributed [38] to their contamination with fragments of the kernels.

On the basis of these observations, it has been concluded [38] that hulls are largely unaffected during extraction of cottonseed with the usual solvents, so that their pigments remain with the meal.

2. Pigmentation of Solvent-Extracted Oils

(a) Influence of Heat on the Color of the Oils. When cottonseed oil extracted with petroleum naphthas is subjected to elevated temperatures during extraction or subsequent removal of the solvent, the color of

[206] K. S. Markley, *J. Am. Soc. Agron.*, **20,** 1102–1107 (1928).
[207] A. H. Gill and H. W. Greenup, *Oil & Fat Ind.*, **5,** 288–294 (1928).

the crude oil is intensified and is not readily removed by refining.[201-204, 208] Podol'skaia and Tobler [208] noted that heating of the crude oil to any temperature above 140° F. (60° C.) caused fixation of color, and the rate of intensification of the color was greatly accelerated at higher temperatures. These observations have been confirmed by Vix *et al.*[202] Similar observations had previously been reported for expressed oils.[23, 136, 209, 210]

Rosenthal reported that the color of oils extracted with liquid propane and butane at very low temperatures is relatively insensitive to heat, whereas the more deeply colored oils extracted with the same solvents at higher temperatures are very sensitive to heat. In order to avoid intensification and fixation of color in the latter oils, the solvent must be removed at temperatures below 210° F.[201]

Fixation of color in crude expressed oils and oils obtained by extraction with petroleum naphtha has been correlated with the gossypol content of the oils. Royce and Lindsay [136, 209] noted that heating of expressed oils reduced the amount of gossypol which could be precipitated from them by aniline. Similar changes were observed [23, 210] when pure gossypol was heated in refined cottonseed oil, and it was found that the color of the solutions alternately increased and decreased as the temperature and the period of heating was increased. Podol'skaia and Tobler [208] observed the same sequence of color changes during heating of crude oils extracted with petroleum naphtha (benzine).

During a systematic investigation of the changes in concentration of gossypol occurring at various stages of processing of cottonseed by extraction with petroleum naphtha, Goldovskii and Podol'skaia [203, 204] observed very little change (Table 94) in the amount of gossypol which could be precipitated with aniline during prolonged extraction at 70° to 80° C., or during removal of the solvent at moderate temperatures. However, considerable decomposition of gossypol occurred upon elevation of the temperature for removal of the last traces of solvent from the oil.

Royce and Lindsay [136, 209] attributed the disappearance of gossypol during heating of expressed oils to its reaction with nitrogenous constituents of the oils, but Podol'skaia [23, 210] observed that gossypol disappeared at the same rate when it was heated in refined cottonseed oil which contained no nitrogen. On the basis of the observation that heating of the solutions in an atmosphere of oxygen or carbon dioxide did not alter the rate of decomposition, Podol'skaia concluded that the reaction did not involve oxidation. Since all solvent-extracted oils contain some gossypol and exposure of the crude oils to some heat can hardly be avoided

[208] M. Z. Podol'skaia and L. Tobler, *Masloboino Zhirovoe Delo,* **16,** No. 4, 5–7 (1940); *Chem. Abst.,* **35,** 924 (1941).

[209] H. D. Royce and F. A. Lindsay, Jr., *Ind. Eng. Chem.,* **25,** 1047–1050 (1933).

[210] M. Z. Podol'skaia, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1936,** 62–70 (English summary, pp. 69–70); *Chem. Abst.,* **32,** 1127 (1938).

during large-scale processing of cottonseed, some fixation of color will always occur. Consequently, determination of the nature of the reaction to serve as a basis for devising methods for removal of the thermally decomposed gossypol is of practical as well as theoretical importance.

TABLE 94

Variation in Gossypol Content of Oil Extracted from Cottonseed with Petroleum Naphtha (Benzine)[a]

Gossypol content, %[b]			
Original meats	Original extract[c]	Extract after partial removal of solvent	Extract after complete removal of solvent[d]
—	0.32	0.32	0.16
1.37	0.38	0.36	0.13
1.51	0.43	0.46	0.14
1.53	0.36	0.31	0.27
—[e]	0.10	0.08	0.06
0.75[e]	0.09	0.13	None

[a] Adapted from A. M. Goldovskii and M. Z. Podol'skaia, *Masloboino Zhirovoe Delo*, **14**, No. 5, 9–12 (1938); *Vsesoyuz. Nauch. Isslodovatel. Inst. Zhirov*, **1939**, 72–83; *Chem. Abst.*, **33**, 5688 (1939).

[b] On a solvent-free basis. [c] Temperature of extraction, 70° to 80°C.

[d] Last traces of solvent removed at an elevated temperature (unspecified) under reduced pressure. [e] Immature (bollie) seed.

Crude oils extracted with diethyl ether have been reported [38] to be almost black, with nearly half of the gossypol decomposed after the extracts had been heated at 220° F. for six hours. Nevertheless, refined and bleached oils of prime colors were obtained by application of the usual methods of refining to the crude extracted oils.

Since extracts obtained with water-miscible alcohols, ketones, and ethers contain nearly all of the pigments of the seed, and these polar solvents constitute very active reaction media, the pigments of the crude oils will decompose readily upon exposure to heat, or even upon standing at low temperatures. However, no systematic investigation appears to have been published concerning the effect of heat on the refining characteristics of crude oils extracted with these solvents.

(b) Refining of Solvent-Extracted Oils. Sievers and McIntyre [191] investigated the refining characteristics of oils extracted at room temperature by a series of organic solvents. All of the crude oils were found to be deeply colored, and they could be refined to the colors shown in Table 95 only with the use of a large excess of alkali.

The crude oils which Shrader [192] obtained by extraction of cottonseed with benzene were reported to require treatment with excess alkali and re-refining in order to produce oils of acceptable color. Wesson [194] reported.

however, that a small-scale pilot plant extraction of cottonseed with benzene yielded an oil which was readily refined to a "good color."

The deeply colored cottonseed oils extracted with chlorinated hydrocarbons have been reported [198] to yield light colored refined oils when the miscella are treated with dilute or concentrated alkali before removal of the solvent.

TABLE 95

Color of Cottonseed Oil Obtained by Extraction with Different Solvents[a]

Refining characteristics of extracted oils	Solvent					
	Diethyl ether	Benzene	Carbon tetrachloride	Trichloro-ethylene	Light gasoline	Heavy gasoline
FFA, %	2.61	1.78	1.36	2.01	1.10	1.08
Ref. loss, %	13.0	10.71	7.87	6.74	10.6	13.51
Type of oil	Lovibond color					
Refined	21.0Y–3.6R	21.0Y–3.9R	32.0Y–2.8R	21.5Y–4.2R	21.7Y–2.5R	24.1Y–4.8R
Bleached	10.4Y–1.8R	14.0Y–2.0R	8.2Y–1.6R	15.0Y–2.6R	8.6Y–2.1R	16.0Y–2.8R
Deodorized	10.4Y–1.0R	15.0Y–1.4R	8.6Y–0.8R	16.0Y–2.4R	13.0Y–1.0R	23.0Y–2.5R

[a] A. F. Sievers and J. D. McIntyre, *Cotton Oil Press*, **4**, No. 10, 44–48 (1921).

TABLE 96

Color of Cottonseed Oil Obtained by Extraction with Liquid Propane and Butane[a]

Solvent	Extraction temperature, °F.	Desolventizing temperature, °F.	Color of oil, Lovibond[b]	
			Refined	Bleached
Propane or butane	−5 to +10	<210	20Y–2.5R[c]	—
Propane	65	190	35Y–3.5R[d]	10Y–0.9R
Butane	<66	190	—	10Y–1.1R

[a] Data from H. Rosenthal, U. S. Pat. 2,254,245 (1941).
[b] Refined and bleached according to official AOCS and NCPA methods.
[c] Sometimes necessary to use stronger lye to obtain oil of 2.5R or lower.
[d] Refining loss 3.3% using 7.7%, 12°Bé. lye.

According to the data of Rosenthal,[201] as shown in Table 96, when cottonseed are extracted with liquid propane or butane at very low temperatures, the oils can be refined to bleached colors by alkali treatment alone, without use of bleaching clays. Final deodorization was reported to be unnecessary because of deodorization during preliminary removal of the solvent with steam at reduced pressures. Oils extracted with the same solvents, but at higher temperatures and desolventized at moderate

temperatures, were refined to prime colors by application of the usual methods designed for expressed oils. When extraction temperatures were in excess of 80° F. or solvents were removed at temperatures above 210° F., the colors of the crude oils were very dark and could not be reduced to an acceptable level by application of the usual refining procedures.

Vix and co-workers [202] have reported (Table 97) that oils extracted with commercial hexane at 70° F. from prime seed were readily refined

TABLE 97

Comparison of Refining Characteristics of Oil Extracted with Commercial Hexane and Hydraulic-Pressed Oil from Prime Seed[a]

Refining lye[b]	Refining loss, %	Colors of oils, Lovibond	
		Refined	Bleached
Oil extracted with hexane:[c]			
12° (80%)	2.9	35Y–4.8R	10Y–0.7R
14° (80%)	3.0	35Y–5.7R	10Y–0.8R
14° (max.)	3.7	35Y–4.8R	10Y–0.8R
16° (max.)	3.6	35Y–4.8R	10Y–0.6R
16° (max.)[d]	4.4	35Y–3.1R	10Y–0.5R
Hydraulic-pressed oil:[e]			
12° (80%)	5.3	35Y–6.8R	20Y–2.3R
14° (80%)	5.7	35Y–6.7R	20Y–1.9R

[a] Data from H. L. E. Vix, E. F. Pollard, J. J. Spadaro, and E. A. Gastrock, *Ind. Eng. Chem.*, **38**, 635–642 (1946).
[b] Oils of 1.4% free fatty acid content; refined according to official AOCS methods.
[c] Solvent stripped from oil with steam at 110°F. and 65 mm. pressure; oil–water emulsion broken by centrifuging.
[d] Slow-break; all others by regular break method. [e] No processing data furnished.

when the solvent was removed at temperatures not exceeding 110° C., and that the refined and bleached oils were more lightly colored than corresponding oils which they had obtained by processing prime cottonseed by the hydraulic-press method. When the extracted crude oils were heated above 150° F. for periods as short as fifteen minutes, their color was intensified and the oils could not be refined to prime colors by any of the methods investigated.

Comparison of the refining characteristics of oils extracted on a small scale from prime cottonseed with diethyl ether and light petroleum naphtha (Skellysolve F) has yielded [38] the results shown in Table 98. Extraction with diethyl ether was continued for twenty-four hours until all but traces of the pigments had been removed from the meal. The extract was refluxed on a steam bath for six hours during the extraction. Extraction with petroleum naphtha was also carried out on a steam bath for a total of six hours, which was the minimum period of time required for complete

TABLE 98

Refining of Cottonseed Oils Extracted with Diethyl Ether and Light Petroleum Naphtha (Skellysolve F)[a]

Solvent	Free fatty acids, %	Lye,[b] °Bé.	Color of oil, Lovibond	
			Refined	Bleached[c]
Diethyl ether	3.5	20	35Y–25.5R	25Y–1.4R
Petroleum naphtha (Skellysolve F)	0.34	20	35Y–7.5R[d]	35Y–5.2R[d]

[a] C. H. Boatner, R. T. O'Connor, C. M. Hall, L. E. Castillon, and M. C. Curet, *J. Am. Oil Chem.* **24**, 276–283 (1947).

[b] Based on amounts required for screw-pressed oils according to official AOCS methods.

[c] Bleached with 6% AOCS official fuller's earth.

[d] Color read on a 1-inch rather than a 5¼-inch column of oil.

extraction in the Soxhlet apparatus employed. The crude oil extracted with diethyl ether was almost black, and was much darker than the oil extracted with petroleum naphtha, but the refined and bleached oils were much lighter than the corresponding refined and bleached oils obtained by extraction of seed with petroleum naphtha.

The absorption spectra of chloroform solutions of the two crude oils (Figs. 82 and 83) demonstrated that they contained entirely different

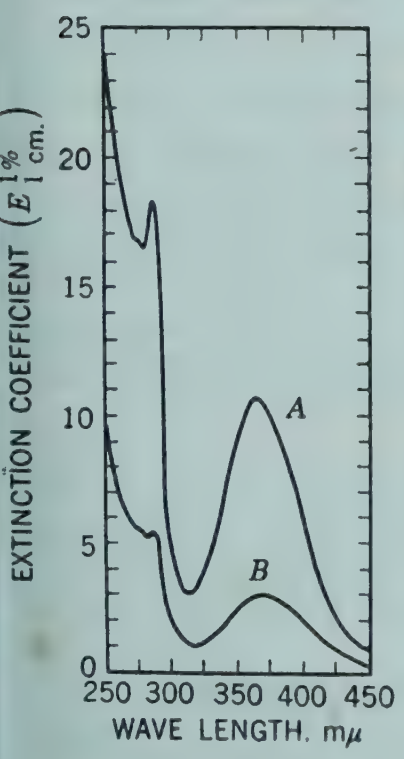


Fig. 82. Absorption spectra of $CHCl_3$ solutions of crude oils extracted from prime cottonseed with (*A*) diethyl ether and (*B*) light petroleum naphtha (Skellysolve F).[38]

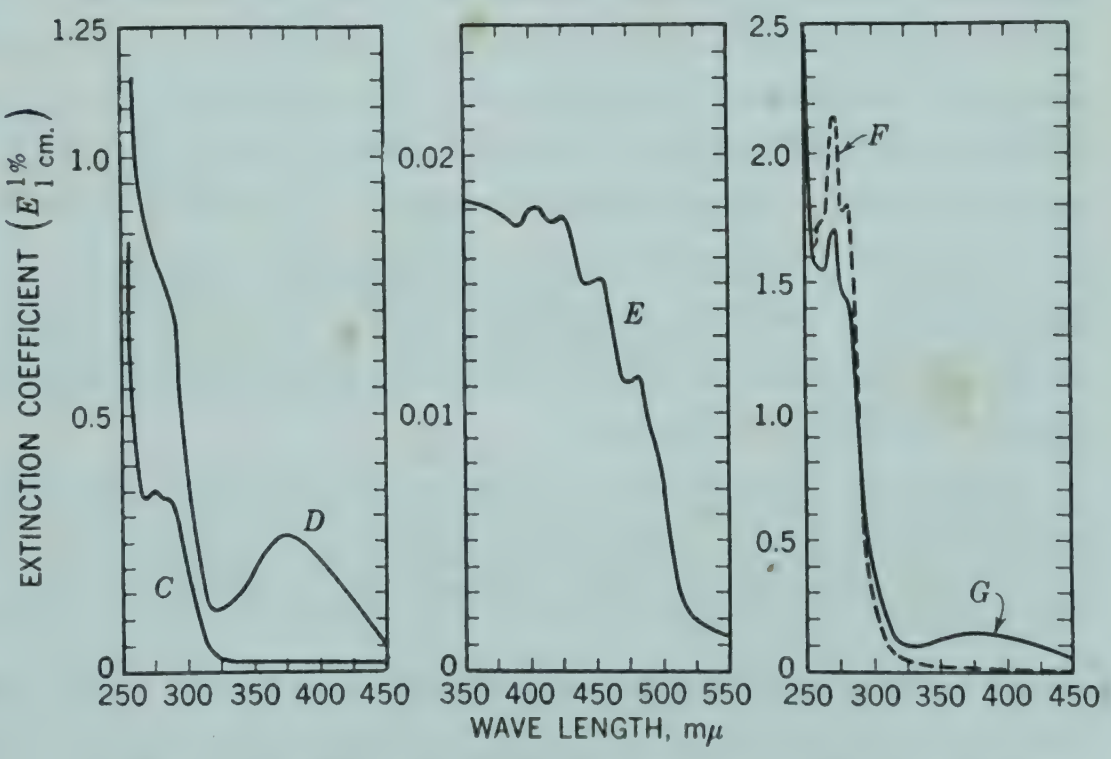


Fig. 83. Absorption spectra of chloroform solutions of bleached and refined oils extracted from prime cottonseed with diethyl ether and light petroleum naphtha (Skellysolve F): *C* and *E*, oil extracted with ether and alkali refined; *D*, oil extracted with petroleum naphtha and alkali refined; *F*, diethyl ether-extracted oil, alkali refined and bleached; *G*, petroleum naphtha-extracted oil, alkali refined and bleached.[38]

pigments. Gossypol was found to constitute 2.16% of the weight of the oil extracted with diethyl ether, even though almost half of the total gossypol extracted had decomposed during the heating of the extract. The crude oil extracted with petroleum naphtha contained a relatively small amount of gossypol (0.33%) and large amounts of the yellow extraglandular pigment.

Alkali refining of the oil obtained with diethyl ether removed all of the gossypol and most of the color, and revealed the presence of pigments which had not previously been detected. These pigments were completely adsorbed during bleaching of the oil, indicating that they are relatively polar compounds. All of the gossypol, but only a fraction of the other pigments, was removed during alkali refining of the crude oil obtained by extraction with petroleum naphtha. The absorption spectrum of the alkali-refined oil resembled that of extracts obtained by extraction of seed with petroleum naphtha in the absence of moisture. Thus, it was concluded that only the extraglandular pigment remained in the oil. Bleaching removed very little of this pigment.

On the basis of these observations, it was concluded that dark colors in crude extracted oils are objectionable only when they are due to relatively stable, nonpolar compounds which are not readily adsorbed during refining and bleaching. Heating of ethereal extracts does not have a deleterious effect on the color of the refined oils because the decomposition products are more readily adsorbed than the original pigments. Since the water-miscible alcohols, ketones, and ethers which extract all of the pigments of the seed with the oil, like diethyl ether, constitute relatively polar reaction media, it was predicted that the coloring matter in oils extracted with these solvents would be readily removed during refining. It was further suggested that preliminary treatment of petroleum naphtha miscella with oxidizing agents would cause decomposition of the pigments to polar compounds which would be removed by adsorption during subsequent refining of the oils.

Olcott [198] has reported that a cottonseed oil extracted from prime cooked seed with petroleum naphtha (Skellysolve A) was similar to hydraulic-pressed oil with respect to its behavior during refining.

3. Pigmentation of Solvent-Extracted Cottonseed Meals

Solvent-extracted cottonseed meals have been found to fall into two categories with respect to the distribution and total content of pigments. Meals obtained by treatment of the seed with water-miscible organic liquids capable of rupturing the pigment glands have been found [38, 39] to contain only the small proportions of the pigments which are insoluble in the solvent mixture employed for extraction of the oil. As shown in Table 99, extraction of cottonseed with acetone or 1,4-dioxane yields

almost colorless meals. Methanol, ethanol, isopropanol, or aqueous mixtures of these solvents rupture all of the pigment glands within a short period of contact and extract all of the gossypol, but only a small amount of gossypurpurin is extracted because of its limited solubility in these solvents. Consequently, extraction with these solvents yields lightly colored meals only when the seed contains very little gossypurpurin, whereas yellow meals colored with the yellow decomposition product of gossypurpurin, such as those shown in Table 99, are obtained from seed which have been stored at moderately elevated temperatures so that they contain moderate amounts of gossypurpurin.

TABLE 99

Color of Solvent-Extracted Cottonseed Meals[a]

Solvent	Visual color of meal	Reflectance[b] at wave lengths indicated, %			
		400 mμ	440 mμ	480 mμ	600 mμ
Aqueous methanol[c]	Light brown	3.2	3.7	11.6	28.0
Aqueous ethanol[c]	Tan	4.5	5.6	16.7	34.0
95% aqueous ethanol	Straw yellow	11.5	15.0	52.5	68.4
Petroleum naphtha (Skellysolve B)	Yellow[d]	12.5	16.6	57.3	72.5
Petroleum naphtha (Skellysolve F)	Pale yellow[d]	13.5	18.0	57.8	72.5
Diethyl ether	Almost white	24.3	38.7	63.5	76.2
Dioxane	White	30.1	41.0	67.0	76.7
Acetone	White	33.7	45.5	72.0	81.8

[a] C. H. Boatner, R. T. O'Connor, C. M. Hall, L. E. Castillon, and M. C. Curet, *J. Am. Oil Chem. Soc.*, **24**, 276–283 (1947).

[b] Measured with General Electric Recording Spectrophotometer on meals ground to pass U.S. No. 100 sieve.

[c] Treated first with an aqueous mixture containing 30% alcohol (by weight); then a more concentrated alcohol mixture was added to yield a final extract of 60% alcohol; the extracted meal was finally washed repeatedly with anhydrous alcohol.

[d] Intact pigment glands throughout tissue.

Since both gossypol and gossypurpurin are somewhat soluble in diethyl ether, and the pigment glands are slowly ruptured by this solvent, a moist commercial-grade diethyl ether can be employed for extraction of the pigments with the oil. However, because of the limited solubility of water in diethyl ether, and the consequent slowness with which the pigment glands are ruptured, meals of the light color shown in Table 99 are obtained only after prolonged periods of extraction.

Meals resulting from the extraction of cottonseed with hydrocarbon solvents fall into a second category. They are usually of the yellow or pale tan color indicated in Table 99. When excessive amounts of moisture and elevated temperatures have been avoided during extraction, most of

the pigment glands remain intact in the meal, and the tissue is colored a pale yellow or tan by adsorption of small amounts of gossypol and the yellow decomposition product of gossypurpurin. Because of the very limited solubility of gossypol and gossypurpurin in the hydrocarbon solvents, only a small fraction of these pigments is extracted with the oil—even when most of the pigment glands are ruptured, as when extraction is carried out in the presence of excessive amounts of moisture and at elevated temperatures. Consequently, cottonseed meals resulting from extraction with hydrocarbon solvents contain most of the original gossypol and gossypurpurin of the seed, and the conditions during extraction determine only whether most of the pigments remain within the intact glands or are adsorbed on the protein tissue.

Olcott [198] has suggested supplementary extraction of defatted meal with diethyl ether in order to remove the residual pigments, but Fontaine, Detwiler, and Irving [211] have reported that extraction of cottonseed with petroleum naphtha followed by exhaustive extraction with diethyl ether yields meals of a distinct yellow color in contrast to the almost colorless meals obtained by direct extraction of cottonseed with diethyl ether alone. The incomplete extraction of the residual gossypol and gossypurpurin of defatted meal accomplished by relatively nonpolar solvents, such as diethyl ether and chloroform,[46] has been shown [38, 39] to be due to the inability of these solvents to elute the absorbed pigments. Goldovskii and Podol'skaia [203, 204] have reported that steaming out of the meal resulting from extraction with petroleum naphtha converts practically all of the residual gossypol to a form which cannot be extracted with diethyl ether.

Treatment of defatted cottonseed with methanol, ethanol, isopropanol, acetone, or 1,4-dioxane has been found [38, 39] to remove both the adsorbed gossypol and that contained in intact glands. The alcohols yield colorless meals only when the gossypurpurin content of the original seed is relatively slight, whereas the meals obtained by final treatment with acetone or 1,4-dioxane are practically colorless, regardless of the pigment content of the original seed or of the defatted meal.

The gland flotation process [41, 212] is applicable for the removal of pigment glands from defatted meal. Thus, when the original extraction with hydrocarbon solvents has been carried out in the presence of little moisture and at moderate temperatures so that most of the gossypol and gossypurpurin have remained segregated in the glands, meals of very little pigmentation are obtained by supplementary application of the flotation process.

[211] T. D. Fontaine, S. B. Detwiler, and G. W. Irving, Jr., *Ind. Eng. Chem.*, **37**, 1232–1236 (1945).

[212] H. L. E. Vix, J. J. Spadaro, R. D. Westbrook, A. J. Crovetto, E. F. Pollard, and E. A. Castrock, *J. Am. Oil Chem. Soc.*, **24**, 228–236 (1947).

Cooking of defatted meal has been reported [16, 198, 213] to produce very little improvement in its nutritional value and presumably very little change in its pigmentation, unless very finely divided meal is cooked for prolonged periods of time in the presence of excessive amounts of moisture.

Although no published data are available concerning meals obtained by extraction of cooked seed with petroleum naphtha, their pigmentation would undoubtedly be determined principally by the conditions under which the seed were cooked, and would probably be very similar to that of hydraulic- and screw-pressed meals obtained from seed cooked under corresponding conditions.

F. The Gland Flotation Process

The recently developed [41] laboratory process of gland flotation for the mechanical separation of most of the cottonseed pigments in the form of intact pigment glands from the oil and meal is based upon the differences in the specific gravities of the glands and other seed tissue, and the resistance of the glands to rupture. The density of the pigment glands (1.26 to 1.38 g. per cc.) is less than that of the extraglandular kernel tissue (1.40 to 1.45 g. per cc.) and of the hulls, the density of which is greater than 1.45 g. per cc. Since the pigment glands are harder than the other parts of the seed tissue, cottonseed kernels can be comminuted to dimensions of the order of magnitude of the glands (diameter, 100 to 400 microns) without rupturing more than a negligible fraction of the latter.

In the application of the gland flotation method for the processing of cottonseed for glands, oil, and meal, the glands are first disengaged from other seed tissue by violent agitation of a suspension of flaked kernels in a solvent or mixture of solvents, such as hydrocarbons, chlorinated hydrocarbons, or glycerides, which do not attack the pigment gland wall. The initial solvent mixture employed for disintegration of the flaked seed can be adjusted to a density of exactly 1.378 g. per cc., or a lighter mixture can be employed, and its density later adjusted to 1.378 g. per cc., for separation of the glands from other seed tissue. The glands which float to the surface are mechanically separated from the dissolved oil and the precipitated gland-free tissue. The tissue is then separated mechanically from the miscella, and the oil is freed of solvent according to conventional methods.

For the processing of seed for glands and gland-free meal after preliminary extraction of the oil with hydrocarbon solvents, contact with moisture must have been avoided during both extraction of the oil and desolventizing of the meal. The same procedure is followed as for non-defatted seed or, alternatively, the defatted meal is first ground to a fine powder and then suspended in the flotation mixture.

[213] H. S. Olcott, U.S. Pat. 2,316,014 (1941).

TABLE 100

Effect of Processing Conditions on Glands, Meals, and Extracts Obtained by the Gland Flotation Process[a]

Sample fractionated	Liquids used for fractionation	Temperature, °C.	Density of mixture, g./cc.	Treatment of suspension	Length of contact, hrs.	Fractions obtained
Hexane-extracted flakes	CCl_4, cottonseed oil	24.5	1.45	Waring Blendor	1.5–2	Yellow liquid; hulls; tissue with glands
Hull-free fraction from C-101	CCl_4, cottonseed oil	24.5	1.36	Waring Blendor	1.5–2	Dark yellow liquid; intact glands; gland-free tissue
Hexane-extracted flakes	CCl_4, cottonseed oil	24.5	1.402	Waring Blendor	1.5–2	Light yellow liquid; intact glands and tissue; gland-free tissue with hulls
Hexane-extracted flakes	CCl_4, cottonseed oil	24.5	1.378	Waring Blendor	1.5–2	Dark yellow liquid; intact glands; gland-free tissue with hulls
Dehulled, ground, and sieved	CCl_4, mineral oil	24.5	1.378	Shaken	1.5–2	Yellow liquid; intact glands; gland-free tissue
Dehulled, ground, and sieved	CCl_4, mineral oil	24.5	1.378	Shaken	1.5–2	Yellow liquid; intact glands; gland-free tissue
Dehulled, ground, and sieved	CCl_4, mineral oil	24.5	1.378	Shaken	1.5–2	Yellow liquid; intact glands; gland-free tissue
Dehulled, ground, and sieved	CCl_4, mineral oil	24.5	1.378	Shaken	1.5–2	Yellow liquid; intact glands; gland-free tissue
Dehulled, ground, and sieved	CCl_4, mineral oil	24.5	1.378	Shaken, rolled on miniature ball mill	1.5–2	Yellow liquid; intact glands; gland-free tissue
Dehulled, ground, and sieved	CCl_4, mineral oil	24.5	1.378	Rolled on miniature ball mill	1.5–2	Yellow liquid; intact glands; gland-free tissue
Hexane-extracted flakes, ground	CCl_4, mineral oil	24.5	1.378	Waring Blendor	24	Cherry red liquid; intact glands; gland-free tissue with hulls

TABLE 100 (*concluded*)

Sample fractionated	Liquids used for fractionation	Temperature, °C.	Density of mixture, g./cc.	Treatment of suspension	Length of contact, hrs.	Fractions obtained
Hexane-extracted flakes, ground	CCl_4, mineral oil	24.5	1.378	Waring Blendor	24	Pink liquid; intact glands; gland-free tissue with hulls
Hexane-extracted flakes, ground	CCl_4, mineral oil	24.5	1.378	Waring Blendor	1.5	Pale pink liquid; intact glands; gland-free tissue with hulls
Hexane-extracted flakes, ground	CCl_4, mineral oil	2.0	1.378	Waring Blendor	1.5	Straw yellow liquid; intact glands; gland-free tissue with hulls
Hexane-extracted flakes, ground, gland-free	CCl_4, mineral oil	24.5	1.45	Waring Blendor	2–3	Very pale yellow liquid; hulls; gland-free, hull-free tissue
Hexane-extracted flakes, ground, gland-free	CCl_4, mineral oil	−29.0	1.446	Shaken	2	Very pale yellow liquid; hulls; gland-free, hull-free tissue
Dehulled and flaked	CCl_4, mineral oil	2.0	1.376	Waring Blendor	2	Yellow liquid; intact glands; gland-free tissue
Petroleum ether-extracted flakes	CCl_4, mineral oil	2.0	1.376	Waring Blendor	2	Yellow liquid; encrusted glands (intact); gland-free tissue
Dehulled and flaked	CCl_4, mineral oil	2.0	1.376	Waring Blendor	2	Yellow liquid; intact glands; gland-free tissue
Petroleum ether-extracted flakes	CCl_4, mineral oil	2.0	1.376	Waring Blendor	2	Yellow liquid; encrusted intact glands; gland-free tissue
Dehulled and flaked	CCl_4, hexane	24.5	1.378	Waring Blendor	2	Pink liquid; intact glands; gland-free tissue

[a] C. H. Boatner and C. M. Hall, *Oil & Soap*, **23**, 123–128 (1946).

1. Pigmentation of the Extracted Oil

Cottonseed oils obtained by direct application of the gland flotation method to the processing of cottonseed for glands, oil, and meal are entirely analogous to the oils obtained by solvent extraction of cottonseed under corresponding conditions. The oils contain all of the soluble extraglandular pigments and varying amounts of the intraglandular pigments.

The fraction of pigment glands ruptured is dependent primarily on the original moisture content of the seed and the amount of moisture in the flaked seed and solvents during flotation. However, as shown by the variation in the color of the extract from yellow, to dark yellow, to pink, to red (Table 100), the number of pigment glands ruptured increases upon prolonging the time of contact or increasing the temperature of the solvent and seed mixture.

On the basis of a semilaboratory development of the gland flotation process, it has been reported [212] that commercial hexane (Skellysolve B) and tetrachloroethylene (perchloroethylene) are the most practical of the various commercially available organic liquids which are suitable for the flotation process.

Drying of flaked seed prior to agitation of the solvent mixture has been found [212] not only to reduce rupture of the pigment glands during flotation, but also to facilitate disintegration of the flakes.

As in the case of oils extracted by conventional methods, the extent of color fixation in the crude oil is determined by the original pigment content of the extract and the temperature at which the solvents are removed. Methods suitable for the refining of oils extracted with dry hydrocarbons and chlorinated hydrocarbon solvents are applicable to oils obtained by the gland flotation process.

2. Pigmentation of the Gland-Free Flour

By preliminary desiccation of the seed before flaking, removal of all moisture from the solvents, and violent agitation of the suspended flakes until all of the glands are detached from other tissue, it should be possible to obtain meals essentially free of color. In actual practice, however, processing of seed of normal moisture content has yielded [41, 212] meals of a very pale yellow color. Agitation of a suspension of flakes of 0.006- to 0.008-inch thickness for a total of eight minutes in a Waring Blendor at high speed, or equivalent agitation with other devices has been found to be required in order to obtain meals essentially free of pigment glands. Processing of seed of normal moisture content yields pale yellow meals containing relatively small amounts, 0.006–0.039% of adsorbed gossypol.

Because of the practical difficulties involved in excluding all moisture during solvent extraction of cottonseed oil with hydrocarbon solvents,

and the consequent adsorption of some gossypol and gossypurpurin on the defatted meals, it has not been possible to obtain as lightly pigmented meals by application of the gland flotation process to defatted meals as are obtained by direct processing of nondefatted seed. As previously pointed out, intact pigment glands are readily separated from defatted meal, but the solvents employed for the flotation process have no effect on pigments adsorbed on the protein tissue.

Adsorbed gossypol has been reported [38, 39] to be eluted from gland-free cottonseed flour by treatment with methanol, ethanol, 1,4-dioxane, acetone, or aqueous mixtures of these solvents. When relatively large amounts of the yellow decomposition product of gossypurpurin are adsorbed, the flour must be extracted with dioxane or acetone in order to free it completely of color.

3. Separated Pigment Glands

Pigment glands separated from cottonseed by the flotation process have been shown [41] to suffer no detectable alteration during their isolation. The glands can be obtained essentially free of adhering tissue by prolonged agitation of the suspended flakes. It has been found,[212] however, that gland-free meal and lightly colored oil can be obtained by less prolonged agitation than that required for freeing the glands of all traces of adhering tissue. The separated glands are then reprocessed by agitating them with finely divided silica (300 mesh) suspended in a dry hydrocarbon solvent. This treatment has been reported to cut nearly all of the remaining extraglandular tissue from the glands and to have little effect on the glands themselves, other than removing a small amount of the external cutin layer of the wall.

The yield of pigment glands obtained by the flotation process is

TABLE 101

Yields of Pigment Glands Obtained by the Gland Flotation Process[a]

Type of seed processed	Moisture content of flaked seed, %		Gland yield, %	
	Original	After drying	Actual[b]	Theoretical[c]
Commercial, prime	7.4	Not dried	1.94	—
Commercial, prime	7.3	4.4	2.73	—
Pure-bred, D & PL[d]	7.6	5.2	2.18	2.92
Pure-bred, Delfos[d]	9.5	5.5	1.96	2.37

[a] Data from H. L. E. Vix, J. J. Spadaro, R. D. Westbrook, A. J. Covetto, E. F. Pollard, and E. A. Gastrock, *J. Am. Oil Chem. Soc.*, **24**, 228–236 (1947).

[b] Calculated on the basis of weight of flakes processed.

[c] Calculated on the basis of gossypol content of flakes and of separated pigment glands.[39] Theoretical yield of glands in commercial seed not calculated because of heterogeneity of original flake lots.

[d] Stored 2½ years before processing.

limited by the gland content of the seed processed, and this has been found (Table 72, page 295) to vary within wide limits, *i.e.*, from 2.4 to 4.8%, in different samples of cottonseed. The presence of moisture in the seed before flaking, and in the flakes and solvent mixtures employed for flotation causes considerable reduction in yields, but, as shown in Table 101, relatively high yields of glands have been obtained [212] on a semilaboratory scale with commercial hexane (Skellysolve B) and tetrachloroethylene, by drying the flaked seed before processing.

Pigment glands separated by the gland flotation process from defatted cottonseed meal are usually heavily encrusted with a layer of finely divided tissue which cannot readily be removed. The encrustation has been found [41] to be particularly heavy when the dry defatted meal is ground before suspending it in the solvent mixture for removal of the glands.

The gossypol content of pigment glands separated from different samples of cottonseed has been found (Table 72, page 295) to vary from 35 to 50%; and the gossypurpurin content, from 0.055 to 1.73%. No other pigments have been detected in the limited number of samples of pigment glands which have been analyzed. Because of the high concentration of gossypol in the pigment glands, and the ease with which it is freed of accompanying impurities (see page 218), separated pigment glands constitute an excellent source of this pigment. Commercial application of the gland flotation process would yield about 25,000 tons of gossypol annually.

G. Possible Uses for the Cottonseed Pigments

The earliest investigators of the cottonseed pigments concentrated their efforts on the development of dyes from the pigments. Kuhlmann [97] was unable to obtain a dye from gossycaerulin which was fast to light. Longmore [18] reported that the yellow pigment which he isolated from the foots from cottonseed oil could be applied as a direct dye for silk and wool, and as a mordant dye for wool. Marchlewski obtained two patents for the preparation of brown mordant dyes from gossypol. According to one process,[214] an alkaline solution of gossypol was oxidized by means of a current of air to yield a brown dye which was reported to be applicable to fabric with basic mordants. According to the second patent,[215] a brown mordant dye was obtained by reaction of gossypol which aromatic nitroso compounds and subsequent sulfonation of the reaction products. Since none of these dyes has been applied on a commercial scale, they would appear to have proved unsatisfactory. However, the afore-mentioned investigations were carried out during the early development of the synthetic dye industry; the possibilities of developing satisfactory dyes

[214] L. P. Marchlewski, E. S. Wilson, and E. Steward, Brit. Pat. 24,418 (1895); *Chem. Zentr.*, **II**, 838 (1889).

[215] L. P. Marchlewski, E. S. Wilson, and E. Steward, German Pat. 98,586 (1897); *Chem. Zentr.*, **II**, 948 (1898).

from gossypol or its derivatives do not appear to have been explored in more recent times.

Gossypol has been reported by Mattill [17] to be one of the most active of the naturally occurring antioxidants of vegetable origin, and his observations have been confirmed by a number of other investigators.[30, 57, 136, 211, 216, 217] The supposed toxicity of gossypol has prevented its use in edible products,[216] but Hove and Hove [30, 57, 217] have reported that gossypol is effective as an antioxidant in lower concentrations than those which have been reported to produce deleterious physiological effects. The latter investigators found that the antioxidant activity of dianilinogossypol, which is physiologically inert, is equal to that of gossypol on a molar basis. Royce [216] has also pointed out the probable usefulness of gossypol as an antioxidant in nonedible products, such as petroleum and rubber products.

Addition of gossypol to expressed oils in concentrations as low as 0.1% has been reported [211] to produce lowered refining losses because of the formation of more compact foots. Gossypol has also been found [203, 204] to act as a refining aid for oils obtained by reprocessing Skipin meals.

Because of its polyphenolic structure, gossypol should also be useful in the field of plastics and drying oils.

Although gossypol has usually been assumed to be a metabolic by-product of the seed, the appearance in all parts of the cotton plant of pigment glands containing little or no gossypol [12] indicates that this pigment participates in the metabolism of the germinating seed or of the developing seedling. Hence gossypol might have a useful effect on the germination or growth of other plants. Application of gossypol to germinating mustard plants has been reported [218] to cause stimulation of germination, particularly in the presence of copper or manganese.

The polyphenolic structure of gossypol and its naturally occurring derivatives suggests their application as pharmaceuticals. An alcoholic extract of cotton-root bark has long been accepted as an emmenagogue and antihemorrhagic.[219–221] Several pigments other than gossypol have been detected in cotton-root bark,[219, 220, 222] but attempts to isolate and identify the component responsible for the physiological activity of the extract have been unsuccessful. However, the observation [40] that gossypol occurs in relatively high concentrations in cotton-root bark suggests that this pigment or one of its conversion products may be the active component of the alcoholic extract.

[216] H. D. Royce, *Oil & Soap,* **10,** 123–125 (1933).
[217] E. L. Hove, *J. Biol. Chem.,* **156,** 633–642 (1944).
[218] J. R. Piland and L. G. Willis, *J. Am. Soc. Agron.,* **29,** 324–331 (1937).
[219] E. S. Wayne, *Am. J. Pharm.,* **44,** 289–291 (1872).
[220] F. B. Power and H. Browning, Jr., *Pharm. J.,* **93,** 420–423 (1914).
[221] *Merck Index,* 5th ed., 1940, p. 170.
[222] H. V. Jordan, D. R. Ergle, J. H. Hunter, and J. E. Adams, *Science,* **86,** 60–61 (1937).

CHAPTER VII

COTTONSEED OIL

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I. Introduction

Cottonseed oil is a member of that particularly useful group of vegetable oils whose fatty acids consist substantially of C_{16} and C_{18} acids containing no more than two double bonds. Its characteristics make it a highly desirable edible oil, hence it is principally used in the manufacture of salad and cooking oils, shortenings, and margarine.

In a discussion of the composition and characteristics of cottonseed oil, three kinds of oil are to be distinguished. These are (*a*) crude oil, which is the oil as it is expressed from the seed, and the commodity shipped from the oil mills; (*b*) refined oil, or oil which has been freed of most of its nonglyceride constituents by treatment with alkali, with or without subsequent bleaching or deodorization; and (*c*) hydrogenated oil.

In the succeeding portions of this chapter, the section dealing with oil trading will be concerned principally with the crude oil. The composition of both crude and refined oils will be discussed. The section on chemical characteristics will deal only with the refined oil, unless otherwise noted. A complete treatment of the characteristics of hydrogenated cottonseed oil is in reality outside the scope of this chapter. However, for the sake of completeness, certain physical characteristics of the hydrogenated oil will be considered, in connection with those of refined oil.

II. Characteristics Recognized in Oil Trading

A. Rationale of Refining Tests

As will be explained in more detail in Chapter XI, the prices to be paid for shipments of crude cottonseed oil are determined on the basis of standard laboratory refining tests, which predict the yield of refined oil that may be obtained, and the quality of the refined oil, in terms of its color and flavor.

By applying the Wesson method (see page 387) it is possible to make an approximate analysis of a crude oil in terms of its content of neutral oil and of free fatty acids, phosphatides, and other material removable by alkali refining. Unfortunately, however, such analysis does not reveal how much refined oil will be yielded by the crude when the latter is actually processed in the refinery. In addition to free fatty acids, phosphatides, and other impurities removed in refining, there is invariably lost, through saponification and emulsification, a certain amount of neutral oil. This amount is quite variable, according to variability in the surface-active properties of some of the nonglyceride constituents. Similarly, crude oils with similar contents of free fatty acids and total nonoil substances may yield refined oils with very different depths of color. A true indication of the value of the crude product can be obtained, therefore, only by means of small-scale refining tests.

The methods for carrying out refining tests and the trading rules based on the tests are outlined in the rulebook issued annually by the National Cottonseed Products Association.[1] For further discussion of refining tests and trading rules, see pages 530–547.

B. Free Fatty Acid Content

Oil expressed from American cottonseed of the highest quality will have a free fatty acid content of 0.5–0.6%. During good seasons practically all the oil produced over wide areas may contain less than 1.0% free fatty acids. On the other hand, unfavorable climatic conditions may cause the oil from an entire cotton-growing state to average 5.0% or higher in free acids. Dry weather during the cotton picking season favors the production of low free fatty acid oil. The oil in moist seed undergoes rapid hydrolysis, whether the seed be stored or standing in the field. Extremely bad oil may contain 15–25% of free fatty acids.

C. Refining Loss

As stated previously, the laboratory refining loss of cottonseed oil depends not only upon the free fatty acid content of the oil, but also upon whether the oil naturally forms firm and nonoily, or soft and oily foots. However, in a large number of samples from different sources a fairly consistent relationship can be observed between free fatty acid content and average refining loss.

The following expression was proposed by Royce and Kibler [2] for the average relationship between refining loss and free fatty acid content in oil from the southeastern United States:

$$\text{per cent refining loss} = 4.25 + 2.3\ (\text{per cent FFA})$$

[1] National Cottonseed Products Association, *Rules Governing Transactions between Members,* issued annually.

[2] H. D. Royce and M. C. Kibler, *Oil & Soap,* **11,** 116–119 (1934).

Probably a better expression for the oils currently produced in the Southeast and the Mississippi Valley is the Barrow-Agee formula:[3]

$$\text{per cent refining loss} = 4.0 + 2.1\ (\text{per cent FFA})$$

Actual experimental results on a number of samples, with an average curve drawn according to this formula, are shown in Figure 84. It will be seen

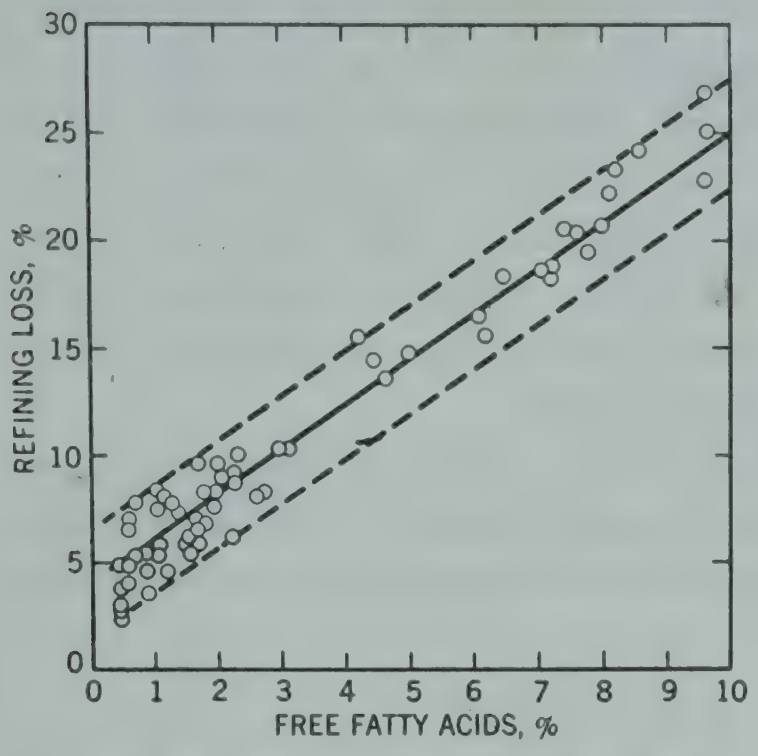


Fig. 84. Relationship between the free fatty acid content and the laboratory refining loss of crude cottonseed oil.

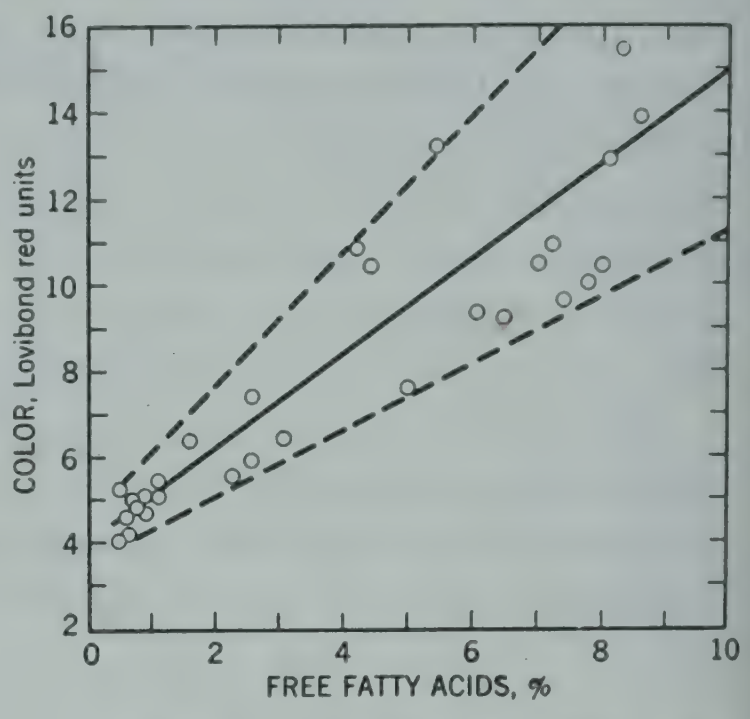


Fig. 85. Relationship between free fatty acid content and refined oil color (lab. settlement tests) in crude cottonseed oil.

that most oils deviate from the mean by not more than ±2.5%. The oils represented in this figure were for the most part reasonably free of meal or other solid material. The presence of excessive amounts of settlings will lead to substantially higher refining losses.

Crude oils from Texas or Oklahoma will generally fall along the upper portion of the above-mentioned diagram, *i.e.*, an average oil with a free fatty acid content of 1.1–1.5%, will have a refining loss of 8–9%.[4] According to Fash,[4, 5] oil from "bollie" or immature cottonseed is exceptionally high in refining loss, and the admixture of 30% or less of such seed with normal seed may lead to the production of oil with a refining loss of 9–11%, at a free fatty acid level of but 1.5%. The refining losses of oil from cottonseed grown on irrigated land in the southwestern United States are comparable to those of oil from the Mississippi Valley or from the southeastern States.[4]

Refining losses as low as 2.5–3.0% are frequently encountered in oils with 0.5–0.6% free fatty acids. Very poor oils (of high free fatty acid

[3] E. R. Barrow, *private communication* (1945).
[4] R. H. Fash, *private communication* (1945).
[5] R. H. Fash, *Oil & Soap*, **11**, 106 (1934).

content) may have refining losses as high as 40–50%. "Basis prime crude," which is the oil tenderable on most contracts, cannot have a refining loss exceeding 16%. The grade known as "off crude" must have a refining loss not exceeding 25%, and in "reddish off crude" the loss must not exceed 40%. No maximum refining loss is specified for "low grade cottonseed oil."

The trading rules specify two alternative methods for conducting refining tests, the "regular" method and the "slow-break" method. Cottonseed oil from most of the producing area of the United States is variable with respect to the method producing the lowest refining loss. Mississippi Valley oil usually refines with a lower loss by the slow-breaking method if its free fatty acid content is low, *i.e.*, less than about 2.5%—but with a lower loss by the regular method if its acidity is high.[3] Texas and Oklahoma oils are stated[4] to generally refine with lower losses by the slow-break method.

Relatively little is known regarding the specific nature of the surface-active materials which influence the refining loss. According to Ganucheau and D'Aquin,[6] certain substances appear to favor emulsification and the production of an oily soapstock, whereas others inhibit it. Presumably, those which contribute to high refining losses are of a phosphatidic or proteinaceous nature. The presence of much gossypol in crude oil leads to the production of a firm soapstock and low refining losses.[2, 7] Oil produced by the Russian process of Skipin is said[8] to refine with an extremely low loss, owing to its high gossypol content. The character and amount of surface-active substances in crude oils produced in the United States appear to be determined by the method employed in cooking the seed, as well as by the amount of deterioration that the seeds have suffered up to the time that the oil is expressed.

D. Color

1. Refined Oil Color

The color of refined cottonseed oil is inclined to roughly parallel the free fatty acid content of the crude oil, since deteriorative changes in the seed lead alike to hydrolysis in the oil and the production of oil-soluble pigments.

An idea of the general relationship between refined oil color (laboratory settlement tests) and free fatty acid content may be gained from Figure 85. The solid line drawn in this figure to indicate more or less average colors for given free acid contents is represented by the following equation:

$$\text{color, Lovibond red units} = 4.0 + 1.1\ (\text{per cent FFA})$$

[6] J. J. Ganucheau and E. L. D'Aquin, *Oil & Soap,* **10,** 49–50 (1933).
[7] H. D. Royce and F. A. Lindsey, *Ind. Eng. Chem.,* **25,** 1047–1050 (1933).
[8] A. I. Skipin and M. Sokolova, *Masloboino Zhirovoe Delo,* **10,** No. 8, 4–11 (1934).

Crude oil of "prime" grade, when refined by the official method, must produce an oil with color not in excess of 7.6 red units on the Lovibond scale.[9] Maximum colors for "basis prime crude," "off crude," and "reddish off crude" oils are 12, 20, and 30 red units, respectively. No maximum color is specified for "low grade cottonseed oil."

The peculiar behavior of crude oil from "bollie" seed has been described by Fash.[5] While the freshly expressed oil will yield a refined oil of normal color, storage of the crude causes rapid deterioration in refined oil color. In a typical storage test on oil from 100% bollie seed, there was an increase in color of from 4.8 to 10.9 in a period of thirty days. In some cases an increase in color of as much as 2 red units occurred during shipment of the crude. Mixtures of bollie oil and normal oil exhibited a greater increase in color than could be attributed to the content

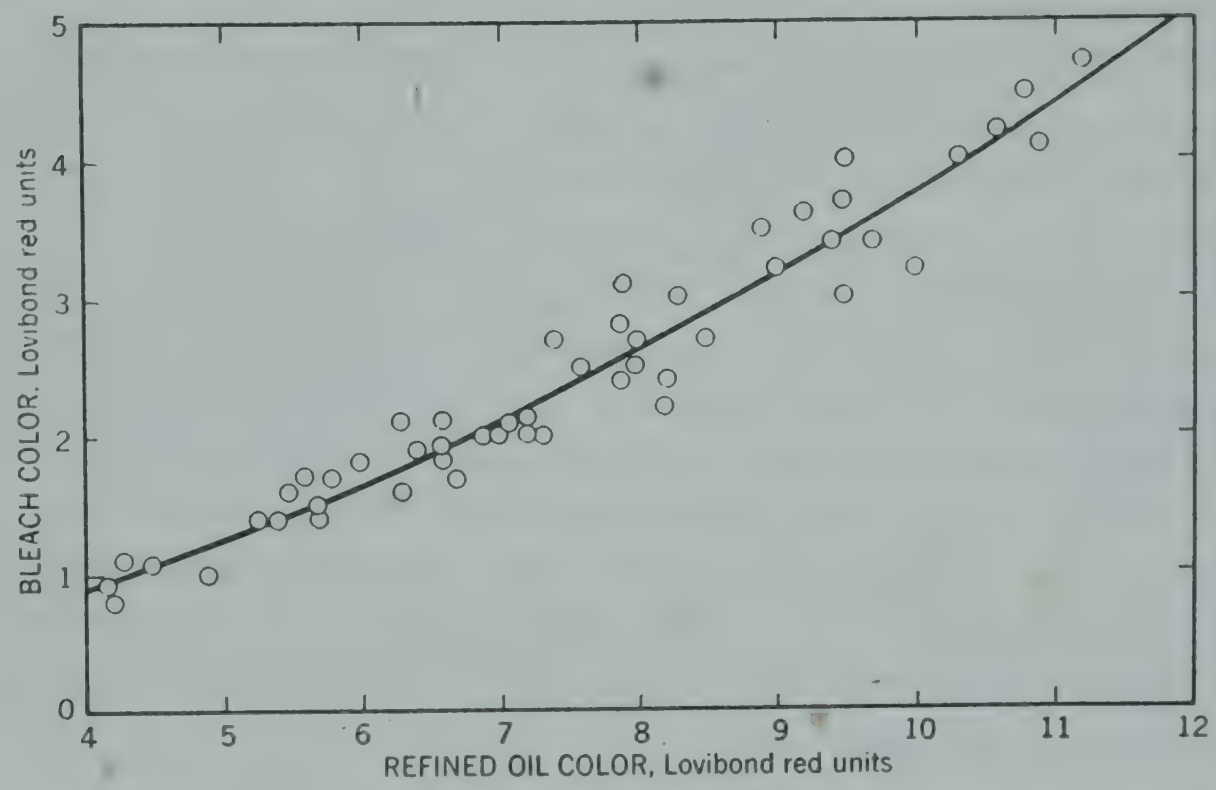


Fig. 86. Relationship between refined oil color and official bleach color of cottonseed oil.

of bollie oil in the mixture, which indicated that constituents of the bollie oil were able to produce a deterioration in the color of normal oil. After refining, bollie oil was stable in color.

Refined oils or "yellow oils" produced from crude oils of good quality may usually be matched with the official Lovibond yellow and red color glasses quite satisfactorily. However, certain oils of poor grade, which contain pigments of a greenish or brownish cast, occasion much difficulty in color evaluation. Even very slight contamination of the crude oil with

[9] The "Lovibond colors" referred to here and elsewhere in the text are, strictly speaking, "N" colors," since the Lovibond glasses used in this country for official color readings must be standardized in terms of the Priest-Gibson N" scale—see K. S. Gibson and G. W. Haupt, *J. Research Natl. Bur. Standards,* **13,** 433–451 (1934); *Oil & Soap,* **11,** 246–250, 257–260 (1934). However, the term "Lovibond color" is almost invariably used in the industry.

fuel oil or other mineral oil will increase the Lovibond red reading of the refined oil greatly.[10] However, this color is readily removable by treatment with carbon. For a discussion of the color of cottonseed oils from the spectral standpoint, see pages 405–407.

2. Refined and Bleached Color

Since refined cottonseed oil is almost invariably subjected to bleaching treatment before it is processed into salad oil, shortening, or margarine, the bleach color of the oil is in reality more important than the refined oil color. Bleaching tests do not figure in the trading rules for crude oils, but a method is provided for determining when a yellow or refined oil is "bleachable." Upon treatment with official fuller's earth under standardized conditions, a bleachable oil must yield a product no darker than 20 yellow, 2.5 red.

The relationship existing between refined oil colors and official bleach colors in representative samples is shown in Figure 86. The average curve drawn in this figure conforms to the equation:

$$B = 0.125Y + 0.025Y^2$$

where B = bleach color, and Y = refined oil color, both being expressed in Lovibond red units.

E. Flavor and Odor

The N.C.P.A. trading rules provide that any crude cottonseed oil which exceeds 3.25% in free fatty acid content shall be automatically graded "Off" in flavor, regardless of its actual flavor and odor. In addition, oil containing less free fatty acids than this *may* be graded "Off," if it is decidedly rancid, musty, sour, bitter, or possessed of a foreign flavor. Actually, oil with less than 3.25% free acids is very seldom assigned an off grade on the score of flavor alone.

F. Variations According to Locality and Season

The different climatic conditions prevailing from season to season produce almost endless variation in the characteristic manner in which each season's oil reacts to the refining tests. Some idea of the variability that may be encountered can be gained from Table 102, in which are compiled certain analytical data on the crude oils received by a refinery in different seasons from Tennessee, Arkansas, Mississippi, and Louisiana.

It may be seen, for example, that during the season of 1932–33, penalties were caused principally by high refining losses. Of 98 tanks of oil penalized, 73 were prime with respect to the color of the refined oil, but were penalized for loss. The following season, 1933–34, presented an

[10] In this connection, see R. H. Fash, *Oil & Soap,* **14,** 241–242 (1937).

TABLE 102

Results of Laboratory Refining Tests[a] on Crude Cottonseed Oil Received at a Single Refinery during Different Seasons (Mississippi Valley Oil)

Measurement	Season					
	1929–30	1930–31	1931–32	1932–33	1933–34	1934–35
Number of tanks	366	320	560	428	449	275
Number under 2.5% FFA	311	249	432	366	423	261
Number over 2.5% FFA	55	71	128	62	26	14
Number not penalized	263	223	405	330	366	214
Number penalized	103	97	155	98	83	61
Number penalized for loss only	52	54	7	73	23	15
Number penalized for color only	5	0	9	8	48	39
Number penalized for both loss and color	46	43	139	17	12	6
Number penalized for flavor only	0	0	0	0	0	1

[a] Figures refer to so-called settlement tests, or the tests which are reported for calculation of penalties and/or premiums, according to the N.C.P.A. rules.

entirely different picture. Out of 83 tanks grading off, more than half, or 48, were off in color but below 9% in loss. In 1931–32 it was rare for oil to be either penalized for loss but not for color, or penalized for color and not for loss. Out of 155 tanks, all but 16 were penalized for *both* loss and color.

In 1930–31 and 1931–32 the number of off tanks of oil exceeded the number having more than 2.5% free fatty acids by only 39 and 21%, respectively. On the other hand, during each of the seasons of 1933–34 and 1934–35 the number of tanks penalized was more than three times the number with free fatty acids in excess of 2.5%.

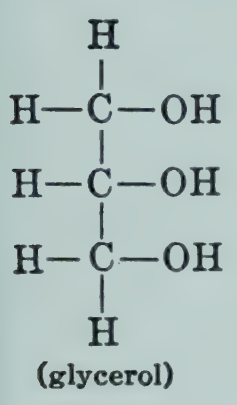
Information on variations in the quality of crude oil according to locality as well as season is furnished by the data collected in Table 103 (see pages 372–373). These represent average results on large numbers of samples examined each season by a commercial laboratory.

III. Composition of Cottonseed Oil

Cottonseed oil, like other common fatty oils, consists predominantly of triglycerides, which are esters of glycerol and a particular class of normal, monobasic, aliphatic acids, known as fatty acids. The fatty acid radicals, being high in molecular weight, make up the greater part of the glyceride molecules, and in addition constitute the most reactive part of the molecules. For this reason, both the chemical and the physical prop-

erties of oils and fats are largely determined by the fatty acids that they contain.

The fatty acids occurring naturally in vegetable oils all have an even number of carbon atoms. The individual fatty acids differ from one another in length of hydrocarbon chain and in the number and position of double bonds in the chain. The relatively high melting and unreactive saturated fatty acids contain no double bonds, in contradistinction to the lower melting and more reactive unsaturated fatty acids, which do have such bonds. The properties of a fat are determined to some extent by the manner in which the fatty acid radicals are grouped by three's in the glyceride molecules. In the latter, the interior position in the molecule is termed the β-position, as distinguished from the outer or α-positions.

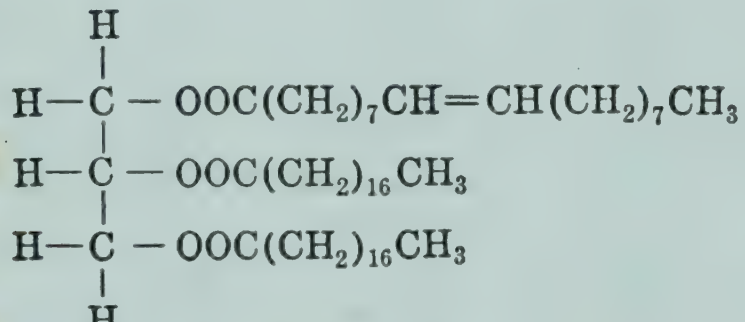


(glycerol)

$CH_3(CH_2)_{14}COOH$
(palmitic acid)

$CH_3(CH_2)_{16}COOH$
(stearic acid)

$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
(oleic acid)



(a triglyceride, α-oleostearin)

In addition to glycerides, crude cottonseed oil contains a certain proportion of fatty acids in the free form, and minor amounts of a variety of other substances, such as phosphatides, sterols, and hydrocarbons. Some of these contribute considerably to the character of the oil. Some are largely or entirely removed in the process of refining, whereas others persist through all common processing treatments.

A. Fatty Acids

The most complete analysis of the fatty acids of cottonseed that has been reported to date is that of Hilditch and Maddison.[11] By careful application of the technique of fractional distillation of methyl esters, supplemented by lead salt separations, these investigators arrived at the composition given in Table 104. In addition to the large proportions of

[11] T. P. Hilditch and L. Maddison, *J. Soc. Chem. Ind.*, **59**, 162–168T (1940).

TABLE 103

Averages of Settlement Refining Test Results on Crude Oils from Four States during Different Seasons[a]

Season	FFA, %	Loss, %	Color, Lov. red units	Percentage of tanks in each grade	
				Prime	Off
Tennessee					
1919–20	7.1	20.4	17.7	6	94
1920–21	1.8	8.9	6.0	88	12
1921–22	2.4	10.1	8.2	65	35
1922–23	1.3	6.5	5.7	75	25
1923–24	2.8	11.5	9.4	26	74
1924–25	1.5	9.8	7.9	65	35
1925–26	9.9	26.4	21.1	3	97
1926–27	4.7	15.1	11.4	31	69
1927–28	1.7	7.1	5.9	97	3
1928–29	1.0	7.2	5.8	95	5
1929–30	1.7	8.5	6.5	78	22
1930–31	1.0	7.8	5.9	96	4
1931–32	2.5	9.6	9.1	52	48
1932–33	1.5	7.8	6.3	91	9
1933–34	1.5	7.8	6.9	83	17
1934–35	1.3	7.6	6.3	93	7
1935–36	0.9	5.9	5.7	85	15
1936–37	1.2	5.9	5.3	100	0
1937–38	1.8	8.2	7.1	65	35
1938–39	1.1	6.3	6.0	86	14
1939–40	0.8	5.8	5.2	97	3
1940–41	1.1	7.1	5.2	97	3
1941–42	1.2	6.6	6.0	89	11
1942–43	0.9	6.6	5.5	87	13
1943–44	1.3	7.8	6.9	80	20
1944–45	1.2	8.1	8.2	79	21
Arkansas					
1919–20	7.6	22.1	16.4	11	89
1920–21	3.7	12.9	9.5	47	53
1921–22	2.2	9.3	7.2	70	30
1922–23	1.1	6.5	6.3	66	33
1923–24	3.6	12.6	8.8	20	80
1924–25	1.0	6.3	5.5	87	13
1925–26	8.5	24.6	19.0	10	90
1926–27	2.4	9.6	7.3	49	51
1927–28	1.2	6.5	5.4	98	2
1928–29	1.0	6.5	5.9	96	4
1929–30	1.1	6.7	5.7	93	7
1930–31	1.0	6.7	5.2	100	0
1931–32	2.2	8.4	8.4	56	44
1932–33	1.2	6.3	5.5	100	0
1933–34	1.8	7.0	7.0	86	14
1934–35	1.3	6.3	5.7	100	0
1935–36	0.8	5.5	4.5	100	0
1936–37	1.0	5.3	5.0	99	1
1937–38	2.6	9.6	8.0	50	50
1938–39	0.8	4.5	5.4	99	1
1939–40	0.7	4.6	4.7	100	0
1940–41	0.9	5.7	4.8	100	0
1941–42	1.2	5.9	5.0	100	0
1942–43	1.1	6.3	5.5	96	4
1943–44	1.0	6.8	5.7	100	0
1944–45	1.0	6.9	4.9	100	0

TABLE 103 (*concluded*)

Season	FFA, %	Loss, %	Color, Lov. red units	Percentage of tanks in each grade	
				Prime	Off
Mississippi					
1919–20	7.5	21.0	15.1	7	93
1920–21	1.9	8.1	6.2	80	20
1921–22	1.8	7.9	6.1	89	11
1922–23	1.3	6.9	5.4	59	41
1923–24	3.2	10.4	8.6	23	57
1924–25	3.0	8.3	6.8	78	22
1925–26	9.3	24.1	15.1	8	92
1926–27	3.1	10.1	8.5	49	51
1927–28	1.8	7.7	6.1	84	16
1928–29	1.3	7.0	5.9	92	8
1929–30	1.7	7.6	6.3	85	15
1930–31	2.1	9.6	6.4	73	27
1931–32	1.9	7.7	7.2	83	17
1932–33	2.1	8.8	6.5	73	27
1933–34	1.8	7.0	6.4	89	11
1934–35	1.6	7.2	5.9	91	9
1935–36	1.4	6.8	5.3	92	8
1936–37	1.1	5.8	5.4	97	3
1937–38	5.4	15.6	10.6	15	85
1938–39	1.5	6.2	6.4	90	10
1939–40	1.1	5.6	5.7	93	7
1940–41	0.8	4.5	5.2	99	1
1941–42	1.9	6.6	6.4	90	10
1942–43	2.0	7.4	6.5	82	18
1943–44	2.1	8.0	6.0	80	20
1944–45	2.4	8.7	7.1	78	22
Louisiana					
1919–20	7.7	21.9	14.4	15	85
1920–21	3.2	10.9	8.2	9	91
1921–22	2.9	10.1	7.7	47	53
1922–23	2.6	11.4	8.6	48	52
1923–24	5.3	15.5	12.3	5	95
1924–25	1.3	7.0	6.2	89	11
1925–26	4.3	13.0	10.0	17	83
1926–27	2.8	9.9	7.4	54	46
1927–28	1.8	7.5	6.2	78	22
1928–29	1.5	7.4	6.1	89	11
1929–30	1.0	6.0	6.2	92	8
1930–31	2.6	10.3	7.7	66	34
1931–32	2.1	8.2	6.7	68	32
1932–33	1.7	6.8	6.1	87	13
1933–34	2.2	7.4	7.5	52	48
1934–35	1.4	6.0	6.4	84	16
1935–36	1.2	5.9	5.5	96	4
1936–37	1.3	5.9	6.0	92	8
1937–38	4.7	13.5	9.3	15	85
1938–39	2.6	7.7	7.1	61	39
1939–40	1.4	6.0	6.3	83	17
1940–41	1.0	5.1	5.9	96	4
1941–42	2.3	8.0	7.0	87	13
1942–43	2.7	9.2	7.5	60	40
1943–44	2.6	9.5	6.9	67	33
1944–45	3.3	10.8	7.6	68	32

[a]Data furnished by Barrow-Agee Laboratories, Memphis, Tenn.

Note: Results during seasons prior to 1927–28 are not strictly intercomparable or comparable to results of subsequent seasons, as standardization of the present refining test method was not achieved until 1927–28.

TABLE 104

The Fatty Acids of Cottonseed Oil of Iodine Value 105.0 and Saponification Equivalent 286.4[a]

Fatty acids	Per cent by weight
Myristic	1.4
Palmitic	23.4
Stearic	1.1
Arachidic	1.3
Myristoleic	0.1
Palmitoleic	2.0
Oleic	22.9
Linoleic	47.8

[a] T. P. Hilditch and L. Maddison, *J. Soc. Chem. Ind.*, **59**, 162–168T (1940).

palmitic, oleic, and linoleic acids and the minor proportions of myristic, stearic, and arachidic acids that cottonseed oil has long been known to contain, this analysis also indicates an appreciable content of palmitoleic (hexadecenoic) acid and a trace of myristoleic (tetradecenoic) acid.

In calculations of the approximate fatty acid composition from iodine and thiocyanogen values, or from iodine values and determinations of total saturated fatty acids, the four saturated acids—myristic, palmitic, stearic, and arachidic—are grouped together, and all the monoethenoid acids are calculated and reported together as "oleic acid." The average composition, on this basis, of oils from the southeastern United States and the Mississippi Valley is about 25% saturated acids, 25% oleic acid, and 50% linoleic acid. This composition corresponds to an iodine value of 108.1. A typical Texas oil, with an iodine value of 102.9, will contain about 27% saturated acids, 27% oleic acid, and 46% linoleic acid. The composition of American oils will seldom fall outside the following limits: saturated acids, 23–28%; oleic acid, 22–28%; linoleic acid, 44–53%.

A paucity of analytical data, as well as the comparative inaccuracy of present analytical methods, has made it impossible to determine whether variations in the total unsaturation of cottonseed oil are reflected in any systematic variation in the proportions of the different fatty acids. More or less definite patterns of variation have been noted in soybean oil [12] and linseed oil,[13] but these oils both vary much more widely in iodine value than does cottonseed oil.

It is entirely possible that cottonseed oil contains traces of fatty acids other than those mentioned above, which have so far escaped detection.

[12] C. R. Scholfield and W. C. Bull, *Oil & Soap*, **21**, 87–89 (1944).
[13] E. P. Painter, *Oil & Soap*, **21**, 343–346 (1944).

The recently developed ultraviolet absorption technique of analysis has revealed that both crude and processed cottonseed oils contain compounds which exhibit triene absorption upon alkali isomerization.[14] These compounds may possibly be trienoic acids, although on the basis of present evidence it appears more likely that they are oxidation products of linoleic acid. The "apparent linolenic acid" content of cottonseed oil is 0.2–0.4%. The isomerizing or dehydrating influence of fuller's earth may produce triene conjugated material in bleached cottonseed oil.[15] The occurrence in cottonseed oil and other seed oils of traces of saturated fatty acids lower than myristic or higher than arachidic is not unlikely. A recent careful analysis of peanut oil,[16] it may be noted, has revealed the presence of minor amounts of caprylic and lauric acids.

The formulas and certain characteristics of the fatty acids occurring in cottonseed oil and other edible oils and fats are listed in Table 105.

B. Glycerides

It has been shown by Hilditch and Jones,[17] and Hilditch and Maddison [11] that cottonseed oil conforms quite closely to the principle of "even distribution" with respect to the manner in which the different fatty acid radicals are grouped in the glyceride molecules. According to these workers, oil of the fatty acid composition shown in Table 104 contains probably 35–40% of palmito-oleolinoleins and about 20% of palmitodilinoleins. Of palmitodioleins, only a minor amount, if any, can be present. Disaturated-monounsaturated glycerides amount to no more than 13–15% of the total, and of trisaturated glycerides there is no more than a trace (*ca.* 0.1%). The remaining 25–30% of triunsaturated glycerides are considered to probably consist largely or entirely of oleodilinoleins. The most probable composition of the oil, according to Hilditch and Maddison,[11] is given in Table 106.

The conclusions of Hilditch and Jones [17] were formulated from the examination of a series of hydrogenated samples of oil; the essentially similar conclusions of Hilditch and Maddison [11] were derived from analyses of the oil after it had been separated into a number of fractions by low-temperature crystallization from a solvent. Since the latter workers could not obtain a fraction with an iodine value higher than that of oleodilinolein (144.2), they concluded that trilinolein probably was not present. However, Riemenschneider *et al.*[18] were able to separate from

[14] R. T. O'Connor, D. C. Heinzelman, and F. G. Dollear, *Oil & Soap,* **22,** 257–263 (1945).

[15] J. H. Mitchell and H. R. Kraybill, *J. Am. Chem. Soc.,* **64,** 988–994 (1942).

[16] H. L. Wikoff, J. M. Kaplan, and A. L. Berman, *J. Biol. Chem.,* **153,** 227–235 (1944).

[17] T. P. Hilditch and E. C. Jones, *J. Soc. Chem. Ind.,* **53,** 13–21T (1934).

[18] R. W. Riemenschneider, C. E. Swift, and C. E. Sando, *Oil & Soap,* **17,** 145–148 (1940).

TABLE 105

Some Commonly Occurring Fatty Acids and Certain of Their Characteristics

Common name	Systematic name	Formula	Molecular wt.	Iodine value	Neutralization value	M. p. °C.	B. p., °C. at 4 mm.
Butyric	Butanoic	$CH_3(CH_2)_2COOH$	88.10	0	636.8	−8	—
Caproic	Hexanoic	$CH_3(CH_2)_4COOH$	116.16	0	483.0	−3.4	83
Caprylic	Octanoic	$CH_3(CH_2)_6COOH$	144.21	0	389.0	16.7	109
Capric	Decanoic	$CH_3(CH_2)_8COOH$	172.26	0	325.7	31.6	133
Lauric	Dodecanoic	$CH_3(CH_2)_{10}COOH$	200.31	0	280.1	44.2	154
Myristic	Tetradecanoic	$CH_3(CH_2)_{12}COOH$	228.36	0	245.7	54.4	174
Palmitic	Hexadecanoic	$CH_3(CH_2)_{14}COOH$	256.42	0	218.8	62.9	192
Stearic	Octadecanoic	$CH_3(CH_2)_{16}COOH$	284.47	0	197.2	69.6	209
Arachidic	Eicosanoic	$CH_3(CH_2)_{18}COOH$	312.52	0	179.5	75.4	—
Behenic	Docosanoic	$CH_3(CH_2)_{20}COOH$	340.57	0	164.7	80.0	—
Lignoceric	Tetracosanoic	$CH_3(CH_2)_{22}COOH$	368.62	0	152.2	84.2	—
Myristoleic	Tetradecenoic	$CH_3(CH_2)_3CH : CH(CH_2)_7COOH$	226.34	112.1	247.9	—	*ca.* 171
Palmitoleic	Hexadecenoic	$CH_3(CH_2)_5CH : CH(CH_2)_7COOH$	254.39	99.78	220.5	—	*ca.* 189
Oleic	Octadecenoic	$CH_3(CH_2)_7CH : CH(CH_2)_7COOH$	282.44	89.87	198.6	16.2	*ca.* 206
Linoleic	Octadecadienoic	$CH_3(CH_2)_4CH : CHCH_2CH : CH(CH_2)_7COOH$	280.43	181.0	200.0	−7	*ca.* 203
Linolenic	Octadecatrienoic	$CH_3CH_2CH : CHCH_2CH : CHCH_2CH : CH(CH_2)_7COOH$	278.41	273.5	201.5	−13	*ca.* 200

TABLE 106

Probable Composition of Glycerides of Cottonseed Oil[a]

Glycerides	Per cent by weight
Tripalmitin	0.1
Oleo disaturated	5.9
Linoleo disaturated	7.3
Monosaturated oleolinolein	40.6
Monosaturated dilinolein	17.8
Oleodilinolein	28.3

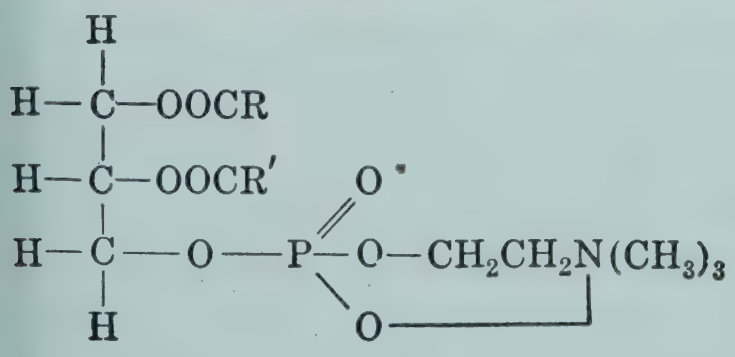
[a] T. P. Hilditch and L. Maddison, *J. Soc. Chem. Ind.*, **59**, 162–168T (1940).

cottonseed oil a fraction amounting to 4.8% of the total which had an iodine value of 148.3, and thus contained trilinolein equivalent to not less than 0.7% of the total glycerides. In addition to trilinolein, Hilditch and Maddison considered it possible, if not probable, that the oil contains minor amounts of monosaturated dioleins and triolein.

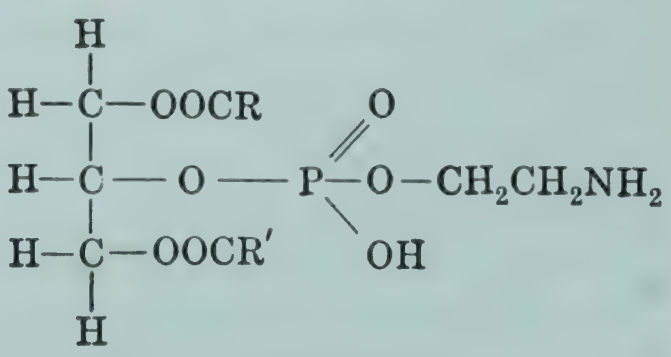
It has been shown by Hilditch and Maddison,[11] and by Meara [19] that—in the palmito-oleostearins, and palmitodioleins of cottonseed oil, cocoa butter, and lard—the palmitic acid radical occupies the inner or β-position in the glyceride molecules. Hilditch and Maddison consider that the monounsaturated-disaturated glycerides of cottonseed oil probably consist for the most part of one of the minor saturated acids (myristic, stearic, arachidic) in combination with palmitic acid and either oleic or linoleic acid.

C. Phosphatides

Phosphatides, which are more or less universally associated with fats and oils in living plants and animals, consist of a polyhydric alcohol



α-Lecithin



β-Cephalin

(usually glycerol), which is esterified with fatty acids, and phosphoric acid combined with a basic, nitrogen-containing component.

The most common phosphatides, lecithin and cephalin, may be considered triglycerides in which one fatty acid radical has been replaced

[19] M. L. Meara, *J. Chem. Soc.*, **1945**, 23–24.

with phosphoric acid. In lecithins, the phosphoric acid is further combined with choline, $HOCH_2CH_2N(CH_3)_3OH$, with a betaine linkage existing between the phosphate and choline radicals. In cephalins, the phosphoric acid is similarly combined with colamine (hydroxyethylamine), $NH_2CH_2CH_2OH$. There are both α- and β-lecithins and cephalins, according to the position of the phosphate radical.

Most of the neutral nonoil material removed from crude cottonseed oil by alkali refining or water washing consists of phosphatides. According to Goldovskii and Liskevich,[20] the amount in either hydraulic-pressed oil oil or solvent-extracted oil is 1.4–1.8%. The "Wesson loss" of American crude oils, which comprises free fatty acids plus phosphatides and other nonoil material removable by refining, is ordinarily 1.0–2.0% greater than the free fatty acid content. Refined and bleached oils contain only traces of phosphatides.

In commercial preparations, phosphatides may be separated from glycerides and other impurities by virtue of their solubility in ether, petroleum naphtha, or benzene, and their relative insolubility in acetone. It is common analytical practice to further separate the purified material into an alcohol-soluble fraction of "lecithins" and an alcohol-insoluble fraction of "cephalins."

The phosphatides of cottonseed oil have not been investigated with sufficient thoroughness, for their nature to be completely understood. Jamieson and Baughman [21] examined the acetone-insoluble portion of "settlings" from a crude oil. This material, in the form of a bright yellow powder, contained 2.68% phosphorus and 1.71% nitrogen, and in addition the following mineral constituents calculated as oxides: silica, 0.60%; calcium oxide, 0.26%; magnesium oxide, 1.46%; potassium oxide, 1.79%; sodium oxide, 0.33%; and ferric oxide, a trace. Associated with the material were carbohydrates which were calculated as 4.2% raffinose and 1.74% pentosans.

Thurman [22] has reported that the acetone-insoluble portion of a commercial preparation [23] contained 2.6–2.9% phosphorus, 0.96% nitrogen, and also 2.6% of a bound sugar. Hilditch and Zaky [24] found that a purified material contained 2.8% phosphorus and 1.6% nitrogen. Upon hydrolysis it yielded 48% of fatty acids of the composition given in Table 107. Rewald [25] found the alcohol-soluble and alcohol-insoluble fractions of cottonseed oil phosphatides to contain, respectively, 3.52 and 4.00% phosphorus. On the basis of their solubility in hot alcohol, he con-

[20] A. M. Goldovskii and M. I. Liskevich, *Trudy VNIIZh*, **1939,** 118–125.
[21] G. S. Jamieson and W. F. Baughman, *J. Oil & Fat Ind.*, **3,** 347–355 (1926).
[22] B. H. Thurman (to Refining, Inc.), U.S. Pat. 2,201,061 (1940).
[23] Obtained by washing the crude oil with a weak boric acid solution—see B. H. Thurman (to Refining, Inc.), U.S. Pat. 2,201,063 (1940).
[24] T. P. Hilditch and Y. A. H. Zaky, *Biochem J.*, **36,** 815–821 (1942).
[25] B. Rewald, *Biochem J.*, **36,** 822–824 (1942).

TABLE 107

Component Fatty Acids of Phosphatides from Cottonseed Oil

Fatty acid	Per cent by weight
Palmitic	17.3
Stearic	7.3
Arachidic	2.8
Palmitoleic	1.5
Oleic	20.3
Linoleic	44.4
Unsaturated C_{20} and C_{22}	6.4

[a] T. P. Hilditch and Y. A. H. Zaky, *Biochem. J.*, **36,** 815–821 (1942).

cluded that the phosphatides consisted of lecithins and cephalins in the ratio of 2–3 to 1.

From a commercial product,[22] Olcott [26] obtained 54% of purified phosphatides. This material consisted of a bright yellow, powdery solid which, unlike soybean phosphatides, was relatively stable. It contained 2.9% phosphorus and 1.2% nitrogen, and yielded 48% fatty acids (iodine value, 100) and an ash of 10–11%. Repeated extraction of the material with hot alcohol yielded a soluble fraction amounting to 15–20% of the total, which contained 3.1% phosphorus, 1.5% nitrogen, and 2.5% ash.

After either acid or alkaline hydrolysis, 41% of the nitrogen in the purified material was in the amino form. The material was readily soluble in water, and in ether or petroleum ether after small amounts of water had been added. It possessed marked antioxygenic activity when tested in a substrate consisting of the ethyl esters of mixed cottonseed oil fatty acids.

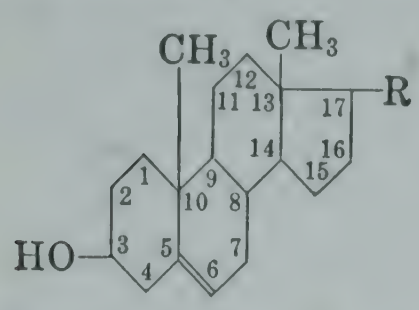
Since pure lecithin containing equivalent fatty acids would yield the considerably different analysis of about 4.0% phosphorus, 1.8% nitrogen, 70% fatty acids, and no ash, Olcott suggested that the phosphatides of cottonseed oil do not consist predominantly of lecithins and cephalins, but rather of compounds more akin to the "lipositol" isolated by Woolley [27] from soybean oil. In lipositol, the polyhydric alcohol with which the fatty acids are esterified, consists—not of glycerol—but of the cyclic alcohol inositol, $C_6H_6(OH)_6$. Also esterified with the alcohol, or otherwise combined, are phosphoric acid, ethanolamine tartrate, and galactose.

D. Sterols

The sterols, which are found in all fats and oils, have the basic structure indicated in the accompanying formula. The individual sterols differ in the side chain designated as R.

[26] H. S. Olcott, *Science*, **100,** 226–227 (1944).
[27] D. W. Woolley, *J. Biol. Chem.*, **147,** 581–591 (1943).

The sterols peculiar to vegetable oils consist of a number of chemical individuals, which have together been given the name of phytosterols.



Basic sterol structure

Among the phytosterols which have thus far been positively characterized are stigmasterol, $C_{29}H_{47}OH$, in which R has the form, —$CH(CH_3)CH{:}\ CHCH(C_2H_5)CH(CH_3)_2$; and β-sitosterol, $C_{29}H_{49}OH$, which is 22,23-dihydrostigmasterol, or stigmasterol to which two hydrogen atoms have been added, to eliminate the double bond in the side chain.[28, 29]

γ-Sitosterol is considered to be probably an isomer of β-sitosterol. a-Sitosterol, once thought an isomer of β- and γ-sitosterols, has been shown by Wallis and co-workers [29-32] to be a mixture of at least three different members, which have been designated α_1-, α_2-, and α_3-.

TABLE 108

Melting Point and Specific Rotation of Sterols from Cottonseed Oil[a]

Sterol	Melting point, °C.	$[\alpha]_D^{25}$
Free stigmastanol	135.5–137.0	—
Acetate	129–130	−14.8
Free β-sitosterol	136–137	−36.6
Acetate	125–126	−41.0
Benzoate	146–147	−13.8
m-Dinitrobenzoate	202–203	−10.4

[a] E. S. Wallis and P. N. Chakravorty, *J. Org. Chem.*, **2**, 335–340 (1937).

According to the probable structure assigned by Bernstein and Wallis,[31] α_1-sitosterol has double bonds between both the 5th and 6th and the 8th and 14th carbon atoms, and a side chain R, which is the same as that of β-sitosterol. It is thus isomeric with stigmasterol, but has its second double bond in the aromatic nucleus rather than in the side chain. α_2-Sitosterol is believed to be probably a homolog ($C_{30}H_{49}OH$) of α_1-sitosterol or of stigmasterol.[30] α_3-Sitosterol is believed to be an isomer of α_1-sitosterol.[32]

According to Kaufmann,[33] crude cottonseed oil may contain up to 1.6% sterols. The sterol content is somewhat reduced by refining; refined oils of American origin usually contain 0.6–1.0% unsaponifiable matter, which consists largely of sterols.

Wallis and Chakravorty [34] have carried out an exhaustive investiga-

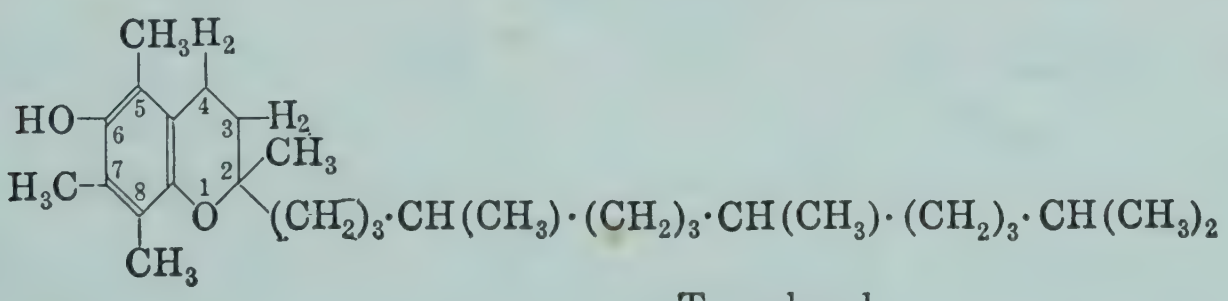
[28] B. E. Bengtsson, *Z. physiol. Chem.*, **237**, 46–51 (1935).
[29] S. Bernstein and E. S. Wallis, *J. Org. Chem.*, **2**, 341–345 (1937).
[30] E. S. Wallis and E. Fernholz, *J. Am. Chem. Soc.*, **58**, 2446–2448 (1936).
[31] S. Bernstein and E. S. Wallis, *J. Am. Chem. Soc.*, **61**, 2308–2313 (1939).
[32] S. Bernstein and E. S. Wallis, *J. Am. Chem. Soc.*, **61**, 1903–1904 (1939).
[33] H. P. Kaufmann, *Fette u. Seifen*, **48**, 53–59 (1941).
[34] E. S. Wallis and P. N. Chakravorty, *J. Org. Chem.*, **2**, 335–340 (1937).

tion of the nature of cottonseed oil sterols, in the course of which some 100 fractional crystallizations were made. The mixed sterols were found to consist predominantly of β-sitosterol. Stigmasterol or α_1-, α_2-, or γ-sitosterols could not be detected, even in traces, although 0.9% of stigmastanol was isolated. This latter compound, $C_{29}H_{51}OH$, may be considered structurally as stigmasterol to which four hydrogen atoms have been added, to form a completely saturated compound. In Table 108 are the values found by Wallis and Chakravorty for melting point and optical rotation of the two cottonseed oil sterols and their derivatives.

By chromatographic adsorption, Windaus and Bock [35] were able to isolate from cottonseed oil—ergosterol, $C_{28}H_{43}OH$—which was estimated to constitute 5.0% of the total sterols. Ergosterol has two conjugated double bonds, in the 5,6 and 7,8 positions; and the side chain has the following structure: $—CH(CH_3)CH{:}CHCH(CH_3)CH(CH_3)_2$. It is a provitamin, being converted to a form of vitamin D upon irradiation with ultraviolet light.

E. Tocopherols

The tocopherols are heterocyclic compounds of high molecular weight which are present in all vegetable oils. Four tocopherols have been identified,[36, 36a] and are designated as α-, β-, γ-, and δ-tocopherols. The structural formula of α-tocopherol is shown below; β- and γ-tocopherols



α-Tocopherol

have one less methyl group substituted in the benzene ring—in β-tocopherol the methyl groups are in the 5 and 8 positions and in γ-tocopherol they are in the 7 and 8 positions. δ-Tocopherol is believed to have one methyl group, in the 8 position.[36a]

The tocopherols are powerful antioxidants, and are principally responsible for the high stability of vegetable oil products, as compared with animal fats of equivalent unsaturation. α-Tocopherol is identical with vitamin E; all of the tocopherols were originally believed to have all

[35] A. Windaus and F. Bock, *Z. physiol. Chem.*, **250,** 258–261 (1937).

[36] H. M. Evans, O. H. Emerson, and G. A. Emerson, *J. Biol. Chem.*, **113,** 319–332 (1936). O. H. Emerson, A. Mohammad, and H. M Evans, *ibid.*, **122,** 99–107 (1937).

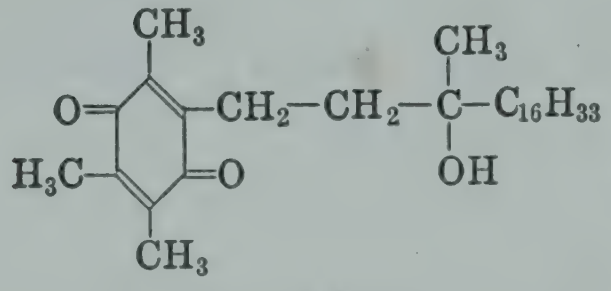
[36a] M. H. Stern, C. D. Robeson, L. Weisler, and J. G. Baxter, *J. Am. Chem. Soc.*, **69,** 869–874 (1947).

manifestations of vitamin E activity, but it has recently been shown [37] that highly purified γ-tocopherol is negligibly active with respect to the prevention of sterility. With respect to antioxygenic activity, however, the potency of the tocopherols increases in the order: $\alpha < \beta < \gamma$.

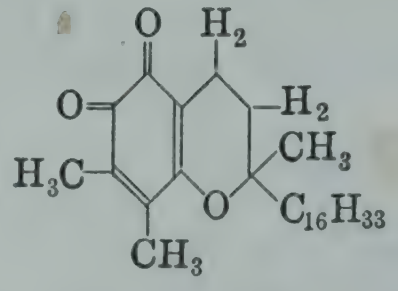
Reported analyses of cottonseed oil for total tocopherols have usually indicated about 0.10–0.14% in the crude, and 0.08–0.12% in the refined oil. However, the Emmerie-Engel method generally employed in the analyses may give slightly high results, since it is responsive to certain easily oxidized substances other than tocopherols. Three samples of refined cottonseed oil examined by Fisher [38] contained 0.060–0.076% α-tocopherol and 0.024–0.034% γ-tocopherol. Cottonseed oil contains a small amount of δ-tocopherol.[36a] β-Tocopherol has as yet not been detected in cottonseed oil, or in fact at the present writing in any oil other than wheat germ oil.

Commercial cottonseed oil products, and particularly those which have suffered some degree of oxidation, may contain considerable amounts of certain oxidation products of the tocopherols.

Mild conditions of oxidation, such as are encountered in an autoxidizing fat, may cause an opening of the heterocyclic ring to form tocoquinones. The same conditions will lead to a conversion of γ-tocopherol, but not



α-Tocoquinone



Chroman-5, 6-quinone

of α- or β-tocopherols, to chroman-5,6-quinone.[39] In the oxidizing crude ethyl esters of hydrogenated cottonseed oil, Golumbic [40] estimated that tocoquinones reached a maximum content of about 0.06% and chroman-5,6-quinone a maximum content of about 0.04%. Swift, Mann, and Fisher [39] have shown that in autoxidizing cottonseed oil there may be formed chroman-5,6-quinone equivalent to as much as 67% of the γ-tocopherol present.

The tocopherols are oily substances,[41] but with certain acids they form crystalline esters. Certain distinguishing characteristics of natural tocopherols and their derivatives are listed in Table 109.

[37] L. Weisler, J. G. Baxter, and M. I. Ludwig, *J. Am. Chem. Soc.*, **67,** 1230–1231 (1945).

[38] G. S. Fisher, *Ind. Eng. Chem., Anal. Ed.*, **17,** 224–227 (1945).

[39] C. E. Swift, G. E. Mann, and G. S. Fisher, *Oil & Soap*, **21,** 317–320 (1944).

[40] C. Golumbic, *Oil & Soap*, **20,** 105–107 (1943).

[41] However, C. D. Robeson, *J. Am. Chem. Soc.*, **65,** 1660 (1943), has reported the crystallization of natural α- and of γ-tocopherols.

TABLE 109

Melting Points, Absorption Maxima, and Extinction Coefficients in Ethyl Alcohol of Natural Tocopherols and Their Esters and of Chroman-5,6-quinone

Compound	M.p., °C.	Absorption max., mμ	$E^{1\%}_{1cm.}$
α-Tocopherol[a]	Oil	292	73.7
α-Allophanate[a]	157–158	286	33.6
α-Palmitate[a]	42–43	286	26.8
α-Acid succinate[a]	76–77	286	38.5
β-Tocopherol[a]	Oil	297	87.6
β-Allophanate[a]	138–139	286	44.5
β-Azobenzene carboxylate[a]	70–71	328	414.0
γ-Tocopherol[b]	Oil	298	94.5
γ-Allophanate[a]	136–138	286	46.0
γ-Palmitate[b]	44–45	286	40.0
δ-Tocopherol	Oil	298	91.2
δ-Phenylazobenzoate[c]	41–42	299	94.0
Chroman-5,6-quinone[d]	Oil	270	136.5
		467	20.0

[a] J. G. Baxter, C. D. Robeson, J. D. Taylor, and R. W. Lehman, *J. Am. Chem. Soc.*, **65**, 918–924 (1943).

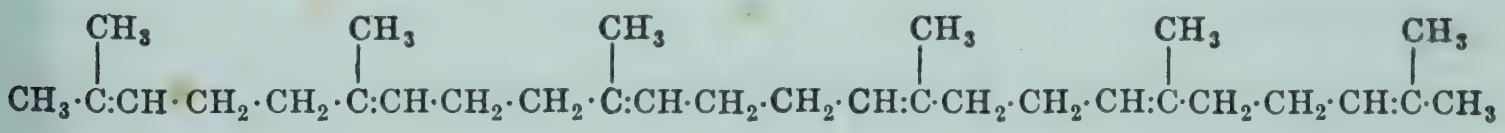
[b] L. Weisler, J. G. Baxter, and M. I. Ludwig, *J. Am. Chem. Soc.*, **67**, 1230–1231 (1945).

[c] M. H. Stern, C. D. Robeson, L. Wesler, and J. G. Baxter, *J. Am. Chem. Soc.*, **69**, 869–874 (1947).

[d] C. E. Swift, G. E. Mann, and G. S. Fisher, *Oil & Soap*, **21**, 317–320 (1944).

F. Hydrocarbons

Squalene, $C_{30}H_{50}$, a highly unsaturated hydrocarbon, is widely distributed in fats and oils. Structurally, it is related to the carotenoids, being made up of six isoprene groups, as shown below. In 12 samples of refined



Squalene

cottonseed oil examined by Fitelson,[42] the content of squalene ranged from 0.004 to 0.012%, with an average content of 0.008%.

The identity of other hydrocarbons occurring in cottonseed oil is not known. According to Kaufman,[33] the total hydrocarbon content of the oil is about 0.25%. Presumably, the hydrocarbon content is unaffected by refining.

G. Pigments

The color of crude cottonseed oil is derived in part from pigments of the gossypol type, and in part from substances of unknown chemical constitution, some of which are probably oxidation or polymerization products

[42] J. Fitelson, *J. Assoc. Official Agr. Chem.*, **26**, 499–511 (1943).

of the gossypol pigments. For a complete discussion of the pigments of crude cottonseed oil, the reader is referred to pages 331–354 of Chapter VI, Pigments of Cottonseed.

Alkali refining removes most of the pigmented materials present in the crude oil, leaving a slight residue of red-yellow color similar to that of other refined seed oils. Careful spectrophotometric examination of most refined oils (see Fig. 92, page 405) reveals absorption maxima at approximately 410, 430, 455, and 480 mμ. It is not known at present whether these represent carotenoid pigments or pigments corresponding more nearly to the gossypol type.

Some of the brownish pigments in oils from damaged seeds may be degradation products of proteins, phosphatides, or carbohydrates. Green pigments of the chlorophyll type occur in crude cottonseed oil,[43] but these, unlike the green pigments of some oils, *e.g.*, soybean oil, are easily removed by refining and bleaching, hence processed oils with a noticeably greenish tinge are practically never encountered.

Most of the color of refined cottonseed oil of good quality may be readily removed by bleaching with fuller's earth, or fuller's earth and carbon; the pigments of oil from damaged seeds are less easily removed by adsorption. Hydrogenation or deodorization affects the pigments of the oil, serving to reduce the color.

Oxidation of refined and bleached cottonseed oil first causes the development of a reddish color, *e.g.*, oil with a Lovibond color of 2 units red may darken to a color of 8–9 units. Following this period of darkening, the oil will bleach to a color lighter than the original, as it becomes strongly rancid. The initial increase in color is caused by the formation of chroman-5,6-quinone, from the oxidation of γ-tocopherol (see preceding section on tocopherols).

H. Other Constituents

The presence of a phytosterolin (sterol glucoside) in cottonseed oil was noted by Jamieson.[21, 44] Thornton, Kraybill, and Broome[45] have more carefully examined 3 g. of this material obtained by adsorption from 36 kg. of oil on an aluminum silicate column. The purified material melted at 248–250° C., and upon hydrolysis yielded *d*-glucose and a sterol fraction which melted at 128–130° C., and had a specific rotation, $[\alpha]_D^{20}$, of -25.07. The sterol acetate had a melting point of 112–114° C., and a specific rotation, $[\alpha]_D^{20}$, of -23.50.

The crude oil contains protein fragments[21] and also resinous and mucilaginous substances which have not been identified.

[43] H. J. McNicholas, *Oil & Soap*, **12**, 167–178 (1935).
[44] G. S. Jamieson, *J. Oil & Fat Ind.*, **3**, 153–155 (1926).
[45] M. H. Thornton, H. R. Kraybill, and F. K. Broome, *J. Am. Chem. Soc.*, **63**, 2079–2080 (1941).

IV. Chemical Characteristics

A. Iodine and Thiocyanogen Values

The *iodine value* is the number of grams of iodine [46] absorbed by 100 g. of oil, and is a measure of the unsaturation or content of double bonds in the oil, one diatomic molecule of halogen being taken up at each double bond.

Cottonseed oil from the southeastern United States or the Mississippi Valley averages about 108 in iodine value, with oil seldom being encountered with a value lower than 104 or higher than 111. Texas oil is somewhat lower in iodine value, averaging about 103. Cottonseed oil, like other seed oils, is inclined to vary in unsaturation according to the latitude in which the plant is grown, with the most unsaturated oils coming from the more northerly regions.[47] However, oil from any part of the United States will almost invariably have an iodine value within the range 100–112.

An iodine value of 108 corresponds ordinarily to a value of about 113 in the mixed fatty acids derived from the oil.

Oil from other cotton-producing regions appears to fall generally within the range of iodine values exhibited by North American oils. Examples of recently reported iodine values of oils from different sources are as follows: African Sudan, 101.8 [48]; Brazil, 105.5 [48]; China, 104.7 [49] and 110 [50]; Russia, 104.2 [51]; and India, 106.4.[52] The values of 112–120 for certain oils of Asiatic origin reported in the older literature [53, 54] do not appear to be representative of modern oils from these regions.

The *thiocyanogen value* is a measure of the thiocyanogen, $(SCN)_2$, absorbed by unsaturated fatty materials—calculation of the value being made in terms of iodine, on the same basis as the iodine value. Since thiocyanogen, unlike iodine, does not add at every bond in the molecule, but only at certain bonds, the thiocyanogen value provides a convenient means

[46] Although calculations are made in terms of iodine, the reagent actually employed in the determination of iodine values is usually a solution of iodine monochloride or iodine monobromide.

[47] H. J. Morrison and L. W. Bosart, *J. Oil & Fat Ind.*, **3,** 130–134 (1926). G. Eckstein, *Industria y quím.*, **5,** 25–34 (1943).

[48] W. G. McLeod, *Oil & Soap,* **15,** 245 (1938).

[49] P. E. Ronzone, *Oil & Soap,* **13,** 165–167 (1936).

[50] Average iodine value of Chinese oil according to Hsi-Pei Fan, Szechuan Oil Mills, *private communication.*

[51] S. L. Ivanov, L. E. Komarova, and A. M. Kogan, *J. Applied Chem. U.S.S.R.,* **7,** 179–186 (1934).

[52] T. P. Hilditch and A. J. Rhead, *J. Soc. Chem. Ind.,* **51,** 198–202T (1932). See also T. P. Hilditch, *The Chemical Constitution of Natural Fats,* Wiley, New York, 1941, p. 138.

[53] K. H. Vakil, *J. Soc. Chem. Ind.,* **36,** 685–692T (1917).

[54] J. I. Lewkowitsch and G. H. Warburton, *Chemical Technology and Analysis of Oils, Fats, and Waxes,* 6th ed., Vol. II, Macmillan, London, 1921, p. 196.

for estimating the composition of fats or their mixed fatty acids. If an oil contains only the saturated acids, oleic acid and linoleic acid, its composition may be calculated from the iodine and thiocyanogen values alone. If, in addition, it contains linolenic acid, these values must be supplemented by a separate determination of the saturated acids.

Formerly it was believed that thiocyanogen added quantitatively at the one double bond of oleic acid, at one of the two double bonds of linoleic acid, and at two of the three double bonds of linolenic acid. It is now known that the addition of thiocyanogen to oleic and linolenic acids is somewhat less than this (it is likewise variable depending upon conditions of the test), and the addition to linoleic acid somewhat greater; consequently, empirical thiocyanogen values must be used if the composition is to be calculated accurately. The values recommended recently [55] by the Fat Analysis Committee of the American Oil Chemists' Society for use in conjunction with the official AOCS method are as follows: for oleic acid, 89.3; linoleic acid, 96.7; linolenic acid, 167.1; olein, 85.5; linolein, 92.5; linolenin, 159.8.

The thiocyanogen value of cottonseed oil, by the AOCS method varies from about 60 to 72, and may be said to average about 65. Corresponding values for the mixed fatty acids are about 63 to 75, and 68.

B. Saponification Value and Related Values

The *saponification value* is the number of milligrams of potassium hydroxide required to saponify one gram of oil. It is a measure, therefore, of the average molecular weight of the glycerides in the oil. The saponification value of pure trimyristin, for example, is 232.8; that of tripalmitin is 208.5; that of tristearin is 188.8, etc. A value generally used by European workers in preference to the saponification value is the *saponification equivalent.* It is defined as the number of grams of fat saponified by one mole or 56.104 g. of potassium hydroxide, and thus in pure triglycerides is numerically equal to one-third the *mean molecular weight* of the glycerides. The relationship between saponification value and saponification equivalent is:

$$[\text{saponification value}] \times [\text{saponification equivalent}] = 56{,}104$$

The *neutralization value* and *neutralization equivalent* bear the same relation to the fatty acids as do the saponification value and saponification equivalent to the glycerides. The neutralization equivalent is numerically equal to the molecular weight of pure fatty acids.

The average saponification value of cottonseed oil is about 195, which corresponds to a saponification equivalent of 288. Extreme values are about 190–198 and 283–295, respectively. Corresponding *theoretical* figures

[55] See *Oil & Soap,* **21,** 143–145 (1944).

for the neutralization value of the fatty acids are 204, average; and extremes, 199–207; and for the neutralization equivalent; average, 275; and extremes, 271–282.

C. Acetyl and Hydroxyl Values

The acetyl and hydroxyl values constitute a measure of the free hydroxyl groups present in oils. The *acetyl value* is the number of milligrams of potassium hydroxide required to neutralize the acetic acid obtained by the saponification of one gram of acetylated oil. The *hydroxyl value* is calculated upon the more rational basis of the weight of the unacetylated oil, and is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of a one-gram sample. The relationship between the two is: $H = A/(1 - 0.00075A)$, where $H =$ hydroxyl value, and $A =$ acetyl value. At low values the two are very nearly equal.

Ordinarily the acetyl value or hydroxyl value of refined cottonseed oil varies from about 8 to 14, although somewhat higher values have been recorded. It is believed that traces of mono- or diglycerides are principally responsible for the presence of free hydroxyl groups.

D. Volatile Fatty Acids

The Reichert-Meissl and Polenske values are determined by empirical tests which give relative figures on the amount of volatile, low molecular fatty acids in oils. The Reichert-Meissl value refers to the steam-volatile acids (chiefly butyric and caproic) which are soluble in water, whereas the Polenske value refers to the volatile water-insoluble acids (chiefly caprylic and capric).

In all fats and oils, except those of the milk fat and coconut or palm kernel groups, these values are very low. Reported values for cottonseed oil are 0.4–0.9 for the Reichert-Meissl value, and 0.2–0.7 for the Polenske value.

E. Neutral Oil Content

An approximation of the content of neutral oil, free of free fatty acids, phosphatides, or other materials reactive with alkali, is furnished by the method devised by Wesson [56] and modified by Jamieson.[57] If the neutral oil content is represented by the equation:

$$N = 100 - (F + I)$$

where $N =$ per cent neutral oil, $F =$ per cent free fatty acids, and $I =$ per cent reactive impurities other than free fatty acids, the value of I will vary from about 0.6 to 2.4, averaging perhaps 1.7.

[56] D. Wesson, *J. Oil & Fat Ind.*, **3**, 297–305 (1926).
[57] G. S. Jamieson, *Vegetable Fats and Oils*, 2nd ed., Reinhold, New York, 1944, pp. 454–455.

The difference between 100 per cent and the per cent neutral oil is sometimes referred to as the "Wesson loss." In refined oils the neutral oil content is, of course, very close to 100 per cent.

F. Glycerol Content

The amount of glycerol yielded by the hydrolysis of refined cottonseed oil varies from about 10.4 to 11.0% of the weight of the oil, averaging about 10.7%. In oils which undergo spontaneous hydrolysis, the glycerol set free appears to be destroyed as rapidly as it is freed, hence the glycerol content of crude oils or foots is dependent upon the neutral oil content. In a neutral oil, the glycerol content in per cent is theoretically equal to 0.0547 times the saponification value.

G. Unsaponifiable Matter

The unsaponifiable material in an oil, as determined by the usual analytical methods, includes sterols, hydrocarbons, tocopherols, and any other materials which after treatment with alcoholic potash are insoluble in water and soluble in ether or petroleum naphtha.

In refined American oils of good quality, the content of unsaponifiable matter is usually 0.5–0.7%. It is a little higher in crude oils, and may be slightly lower in some deodorized products, since alkali refining and high-temperature deodorization are both inclined to effect some removal of sterols, etc. Some foreign oils appear to be higher in unsaponifiable matter, a content of 1.5%, for example, having been reported for a Chinese oil.[49]

H. Halphen Test and Other Color Tests

A very sensitive and reliable means of detecting cottonseed oil is provided by the Halphen test, which depends upon the presence in the oil of chromogenic substances peculiar to the cotton plant and botanically related plants. Of the latter, only the kapok tree produces oil in commercially important quantities. Kapok oil responds to the Halphen test quite as strongly as cottonseed oil, but may be distinguished from cottonseed oil by means of the Besson test.[58]

The Halphen test is capable of detecting 0.25% or less of cottonseed oil in admixture with other oils, and at concentrations of about 0.25–1.00% the depth of color is roughly indicative of the cottonseed oil content.[59] After hydrogenation, cottonseed oil is no longer responsive to the Halphen test. The amount of hydrogenation required to destroy the test is quite variable, according to the conditions of hydrogenation, but may correspond to a reduction in iodine value of no more than 2–5 units. The statement is often made that blowing with air or heating to high temperatures

[58] A. A. Besson, *Chem.-Ztg.*, **38,** 982 (1914). See also V. C. Mehlenbacher, *Oil & Soap,* **14,** 118–119 (1937).

[59] See *Oil & Soap,* **21,** 143–145 (1944).

in the presence of air will cause oils to fail to give the Halphen reaction, but oils so treated will seldom, if ever, be encountered in industrial practice.

Various other color or turbidity tests which have been proposed for the detection of the raw oil or the hydrogenated oil cannot be considered reliable.

I. Keeping Quality

Refined and deodorized cottonseed oil of good quality will ordinarily keep 10–12 hours when tested by the Swift method, wherein the sample is aerated at 97.7° C. Under accelerated conditions of oxidation, cottonseed oil begins to have a rancid odor at a peroxide value (milliequivalents per 1000 g.) of about 125. The keeping time of comparable oil by the Schaal or oven method at 145° F. is 10–12 days. Crude cottonseed oil is considerably more resistant to oxidation than refined oil, and hydrogenation, of course, increases the stability greatly.

Unlike soybean oil, linseed oil, and other vegetable oils containing linolenic acid—cottonseed oil is not subject to that type of deterioration known as flavor reversion.[60]

J. Heating Tests

Since heat is evolved in the reaction of an unsaturated fatty material with bromine, sulfuric acid, etc., a number of thermal tests have been devised for the approximate evaluation of unsaturation in oils. Of these, the best known is the *Maumené test*, which involves reaction of the oil with strong sulfuric acid under standard conditions, and measurement of the ensuing rise in temperature. Maumené values of 75–90° C. have been reported [54] for cottonseed oil. Although once a subject of much interest, thermal tests are now seldom carried out.

The *Mackey test* measures the tendency of an oil spread on cotton waste to oxidize and initiate spontaneous combustion. Refined cottonseed oil heats with comparative readiness under the conditions of the Mackey test,[61, 62] although the crude oil is said to be quite stable.[62]

V. Physical Properties

A. Physical Structure of Cottonseed Oil

1. Structure of the Liquid Oil

It is uncertain to what extent the molecules in liquid fats tend to be associated or grouped in pairs or other aggregates. However, it appears

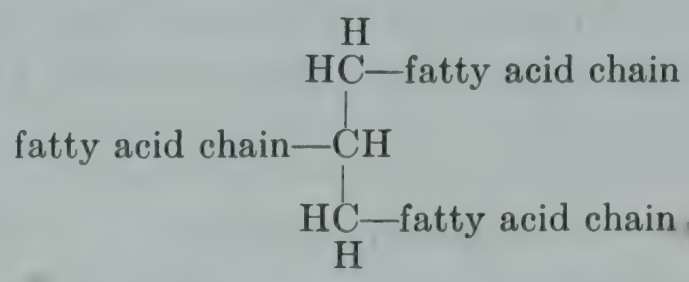
[60] See, for example, A. E. Bailey, *Oil & Soap*, **23**, 55–58 (1946).
[61] N. J. Thompson, *Ind. Eng. Chem.*, **19**, 394–397 (1927).
[62] H. Aspegren, *Oil & Fat Ind.*, **6**, No. 1, 19–23 (1929).

probable that there is some degree of molecular aggregation, since association is common in long-chain compounds.

Cottonseed oil, which has been chilled and partially solidified and then allowed to liquefy at room temperature, will not supercool in the manner of a previously heated oil, but when rechilled will deposit crystals with comparative readiness. This is evidence of the existence in the oil of aggregates, which serve as crystal nuclei, and which are destroyed only by heating the oil considerably above its melting point.

2. Crystal Structure

The crystal structure of fats (triglycerides) may be deduced from their x-ray diffraction patterns. It has been shown by Malkin and co-workers [63] that in crystalline triglycerides the fatty acid chain in the β-position of each molecule extends in a direction opposite to that of the chains in the α-positions:



and that in completely saturated triglycerides the molecules are usually arranged in unit cells to form layers having a depth equal to approximately twice the length of the fatty acid chains (see *A* and *B* of Fig. 87). In the case of saturated fats containing principally C_{18} fatty acids, this depth is about 50 Å., if the chains are arranged vertically in layers. Where the chains are tilted, the depth is of course less. X-ray diffraction measurements give a single *long spacing* corresponding to the depth of the layers, and multiple *short spacings* corresponding to constant and recurrent distances measured between the parallel fatty acid chains.

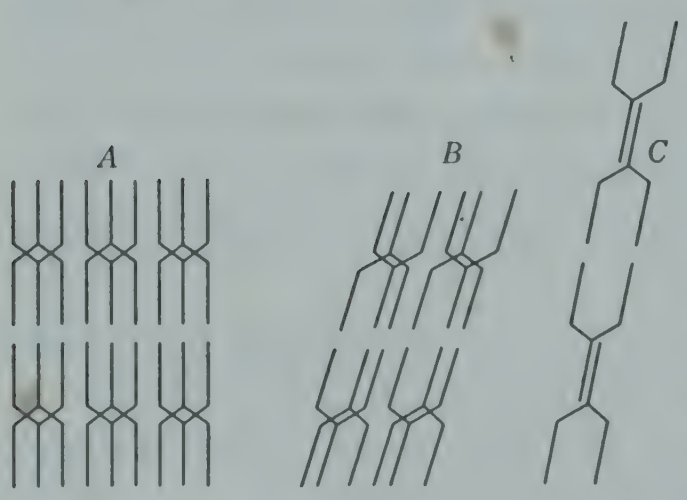


Fig. 87. Diagrammatic representation of crystal structure in triglycerides: (*A*) vertical form of simple saturated triglycerides (alpha form); (*B*) tilted form of simple saturated triglycerides (beta or beta prime forms); (*C*) tilted form of monounsaturated-disaturated glycerides.

Lutton [64] has observed in certain glycerides containing both saturated and unsaturated acids a triple-chain-length structure, the configuration within the crystals apparently being as indicated at *C* in Figure 87.[65]

[63] See C. E. Clarkson and T. Malkin, *J. Chem. Soc.*, **1934,** 666–671.
[64] E. S. Lutton, *J. Am. Chem. Soc.*, **68,** 676–679 (1946).
[65] See also L. J. Filer, Jr., S. S. Sidhu, B. F. Daubert, and H. E. Longenecker, *J. Am. Chem. Soc.*, **68,** 167–171 (1946).

Triglycerides are *polymorphous, i.e.,* capable of crystallizing in different forms, each of which has a distinctive melting point, density, heat of fusion, etc. Polymorphism arises from differences in the degree to which the cells are tilted in the crystal layers (compare *A* and *B,* Fig. 87), and in the manner in which they are packed in the layers; hence each form of a given glyceride has a distinctive pattern of long and short spacings. At a temperature approaching its melting point, each low-melting form tends to undergo spontaneous transformation to a more stable form of higher melting point. However, the glycerides are monotropic; transformations in the reverse direction cannot occur.

Bailey *et al.*[66] found that cottonseed oil which had been hydrogenated to an iodine value of 0.85 could be crystallized in forms with four distinct melting points. However, distinctive x-ray patterns could be obtained for only two forms. The complete x-ray and melting point data are given in Table 110.

TABLE 110

Melting Points and X-Ray Diffraction Characteristics of Highly Hydrogenated Cottonseed Oil (Iodine Value, 0.85)[a]

Form	Melting point, °C.	Long spacing, Å.	Short spacings,[b] Å.
I	62.3	45.3	5.61 (vw), 4.13 (s) 3.73 (m), 3.19 (vw) 3.19 (vw), 2.51 (vw) 2.22 (vw)
II	61.0	[c]	[c]
III	58.5	[c]	[c]
IV	50.5	49.3	4.04 (s)

[a] A. E. Bailey, M. E. Jefferson, F. B. Kreeger, and S. T. Bauer, *Oil & Soap,* **22,** 10–13 (1945).

[b] In reference to intensity of short spacing lines above, s = strong; m = medium; w = weak; vw = very weak.

[c] Distinctive spacings were not observed; pattern was the same as for form I.

Lutton[67] has suggested that forms I, II, and III of Bailey and coworkers may actually be identical with respect to the fundamental crystal structure, small differences in melting point having arisen from varying degrees of "crystal perfection" in the sample. He identifies the above forms with the "beta prime" form of pure triglycerides, and form IV with the "alpha" form of such glycerides.

The lowest melting form of highly hydrogenated cottonseed oil, unlike that of tristearin or other pure triglycerides, is unstable at temperatures considerably below its melting point. At ordinary room temperature, it

[66] A. E. Bailey, M. E. Jefferson, F. B. Kreeger, and S. T. Bauer, *Oil & Soap,* **22,** 10–13 (1945).

[67] E. S. Lutton, *J. Am. Chem. Soc.,* **67,** 524–527 (1945).

transforms to one of the higher melting forms within a matter of a few hours.

B. Oiliness. Viscosity. Surface Properties

The "oiliness" of cottonseed oil and other fatty oils results from the long-chain structure of the glyceride molecules. When a film of oil is interposed between two solid surfaces, the relatively large glyceride molecules prevent the surfaces from coming into close contact, with the establishment of cohesive forces. At the same time, the oil tends to adhere tenaciously to most surfaces, so that it is not easily squeezed or rubbed out.

Cottonseed oil or other edible oils are no longer used as lubricants for machinery, and in fact, fatty oils of any sort have largely been replaced for this service by petroleum products. However, the lubricating action of edible fats and oils is still important in certain applications, particularly in the manufacture of baked goods.

The viscosity of oils, other things being equal, increases with increasing size of the molecules. For this reason, polymerized oils (blown or heat-bodied) are more viscous than normal oils.

TABLE 111

Viscosity of Raw and Hydrogenated Cottonseed Oils[a, b]

Sample number:	1	2	3	4	5	11	12	13	14
Iodine value:	112[c]	108[c]	101[c]	78	66	61	56	28	6
Temperature, °C.	Viscosity, centipoises								
28.5	45.3	45.6	50.8	—	—	—	—	—	—
37.0	32.4	32.8	—	41.7	—	—	—	—	—
47.6	22.8	23.2	25.5	28.5	30.8	31.5	32.4	—	—
67.5	13.4	13.7	14.5	15.8	17.2	17.3	17.6	18.7	20.7
94.7	7.15	7.30	7.85	8.36	8.65	8.99	9.01	9.57	10.22
124.3	4.61	4.65	4.69	4.98	5.18	5.22	5.22	5.49	—
141.8	3.50	3.64	3.71	—	4.01	4.02	—	4.18	4.48
151.2	3.18	3.22	3.26	3.37	3.45	3.50	3.52	3.65	3.88
179.9	2.32	2.36	2.40	2.45	2.48	2.49	2.53	2.64	2.73
203.5	1.88	1.89	1.90	1.94	1.96	1.96	1.99	—	2.08
225.6	—	—	1.58	—	—	—	1.63	—	1.70
244.4	—	—	1.41	—	—	—	—	—	1.46

[a] H. Wakeham and F. C. Magne, *Ind. Eng. Chem.*, **36,** 568–570 (1944).
[b] For densities of these oils, see Table 113, page 394.
[c] Unhydrogenated oils; other samples are hydrogenated oils.

Rescorla and Carnahan [68] examined a sample of cottonseed oil with an acid value of 14.24 (free fatty acid content, 7.2%) and a specific gravity, 20°/4° C., of 0.9187, and reported the following viscosities: at

[68] A. R. Rescorla and F. L. Carnahan, *Ind. Eng. Chem.*, **28,** 1212–1213 (1936).

100° F., 38.88 centistokes and 181 seconds, Saybolt; at 210° F., 8.39 centistokes and 52.7 seconds, Saybolt. Other workers have reported Saybolt viscosities of 56–64 seconds at 210° F. and 184–189 seconds at 100° F., for refined oils.

Recently, Wakeham and Magne [69] have obtained comprehensive viscosity and density data on several samples of refined cottonseed oil and a series of oils hydrogenated to different degrees. Selected portions of their data are presented in Table 111. It is to be noted that the viscosity increases slightly with decreased unsaturation of the oil. Different samples of unhydrogenated and hydrogenated oils of equivalent iodine value were found to agree closely in viscosity.

Magne and Skau [70] have determined the viscosity of winterized cottonseed oil with an iodine value of 110.6, in admixture with acetone, petroleum naphtha (Skellysolve B), and methyl ethyl ketone. Their data for the cottonseed oil–petroleum naphtha mixtures are shown in Table 112.

TABLE 112

Viscosity of Mixtures of Winterized Cottonseed Oil (Iodine Value, 110.6) and Skellysolve B[a]

Per cent by weight of oil	Temperature, °C.					
	−20	−10	0	10	20	30
	Viscosity Centipoises					
0	0.54	0.48	0.43	0.39	0.33	0.29
11.15	0.83	0.71	0.62	0.55	0.46	0.40
19.22	1.12	0.97	0.84	0.74	0.62	0.54
29.06	1.74	1.48	1.25	1.07	0.88	0.74
38.98	2.89	2.32	1.90	1.59	1.26	1.04
49.00	5.46	4.06	3.22	2.64	1.95	1.54
58.28	—	7.14	5.43	4.29	3.01	2.30
71.73	—	18.60	13.00	9.61	6.25	4.50
78.76	—	34.02	22.54	15.84	9.80	6.75
88.00	—	90.4	54.79	34.87	19.91	12.79
100	—	—	198.5	112.3	54.76	31.48

[a] F. C. Magne and E. L. Skau, *Ind. Eng. Chem.*, **37,** 1097–1101(1945). For density data on these mixtures, see Table 114, page 396.

The surface tension of refined cottonseed oil, as measured by the du Nuöy or ring method is about 36 dynes per cm. at 45° C. and about 25 dynes per cm. at 200° C. The interfacial tension of soap-free oil against water at 30–50° C. averages about 29–30 dynes per cm. Partial hydrogenation of the oil has little effect on the surface or interfacial tension.

[69] H. Wakeham and F. C. Magne, *Ind. Eng. Chem.*, **36,** 568–570 (1944).
[70] F. C. Magne and E. L. Skau, *Ind. Eng. Chem.*, **37,** 1097–1101 (1945).

C. Density and Expansibility

The density of liquid cottonseed oil at 15° C. is usually between 0.918 and 0.922. Hydrogenation slightly reduces the density of the liquid oil; the data of Wakeham and Magne [69] for raw and hydrogenated oils over a considerable range of temperature are shown in Table 113. The density

TABLE 113

Density of Raw and Hydrogenated Cottonseed Oils[a]

Sample number:	1	2	3	4	6	12	13	14
Iodine value:	112[b]	108[b]	101[b]	78	65	56	28	6
Temperature, °C.	Density							
29.9	0.9112	0.9105	0.9130	—	—	—	—	—
37.0	0.9068	0.9061	—	0.9031	0.8993	—	—	—
67.5	0.8869	0.8863	0.8883	0.8837	0.8798	0.8783	0.8755	0.8750
100.8	0.8654	0.8649	0.8667	0.8621	0.8584	0.8570	0.8540	0.8533
141.8	0.8389	0.8383	0.8405	0.8360	0.8319	0.8308	0.8280	0.8273
200.2	0.8011	0.7998	0.8050	0.7988	0.7947	0.7938	0.7908	0.7902
233.8	—	—	0.7845	0.7768	—	0.7723	0.7693	0.7683

[a] H. Wakeham and F. C. Magne, *Ind. Eng. Chem.*, **36**, 568–570 (1944).

[b] Unhydrogenated oils; other samples are hydrogenated oils.

of the oil, raw or hydrogenated, changes about 0.000638 for each degree C. change in temperature. At 25° C. (77° F.), therefore, an average cottonseed oil has a density of about 0.914 and weighs about 7.63 pounds per U.S. gallon or 57.5 pounds per cubic foot. Corresponding figures for 100° C. (212° F.) are 0.865, 7.22 pounds, and 54.0 pounds; and for 200° C. (392° F.) 0.801, 6.68 pounds, and 50.0 pounds.

Bailey and Singleton [71] measured the density of hydrogenated cottonseed oils which had been cooled to a sufficiently low temperature to cause complete solidification. The values found at −38° C. were 1.000 for a partially hydrogenated oil (iodine value, 59.5), and 1.022 for an almost completely hydrogenated oil (iodine value, 0.85). The thermal expansibility of the highly hydrogenated oil in a completely solid state was found to be 0.00029 ml. per g. per ° C., and that of the partially hydrogenated oil was less than 0.00039 ml. per g. per ° C. Corresponding expansibilities for the liquid oils immediately above the melting point were 0.00091 for the highly hydrogenated oil and 0.00087 for the partially hydrogenated oil.

The total dilation of the highly hydrogenated oil in changing from a solid at −38.2° C. to a liquid at 74.0° C. was 0.1719 ml. per g.; the corre-

[71] A. E. Bailey and W. S. Singleton, *Oil & Soap*, **22**, 265–271 (1945).

sponding dilation for the partially hydrogenated oil between —38.6° C. and 59.0° C. was 0.1314 ml. per g. The true melting dilation, corresponding to a hypothetical transformation from solid to liquid at a fixed temperature, without premelting, was calculated to be 0.1322 ml. per g. for the highly hydrogenated oil and 0.076 ml. per g. for the partially hydrogenated oil. Calculations of the melting dilation were made at the final melting point (62.5° C.) for the highly hydrogenated oil and at the point of half-fusion (13.8° C.) for the partially hydrogenated oil (see Fig. 88). All of

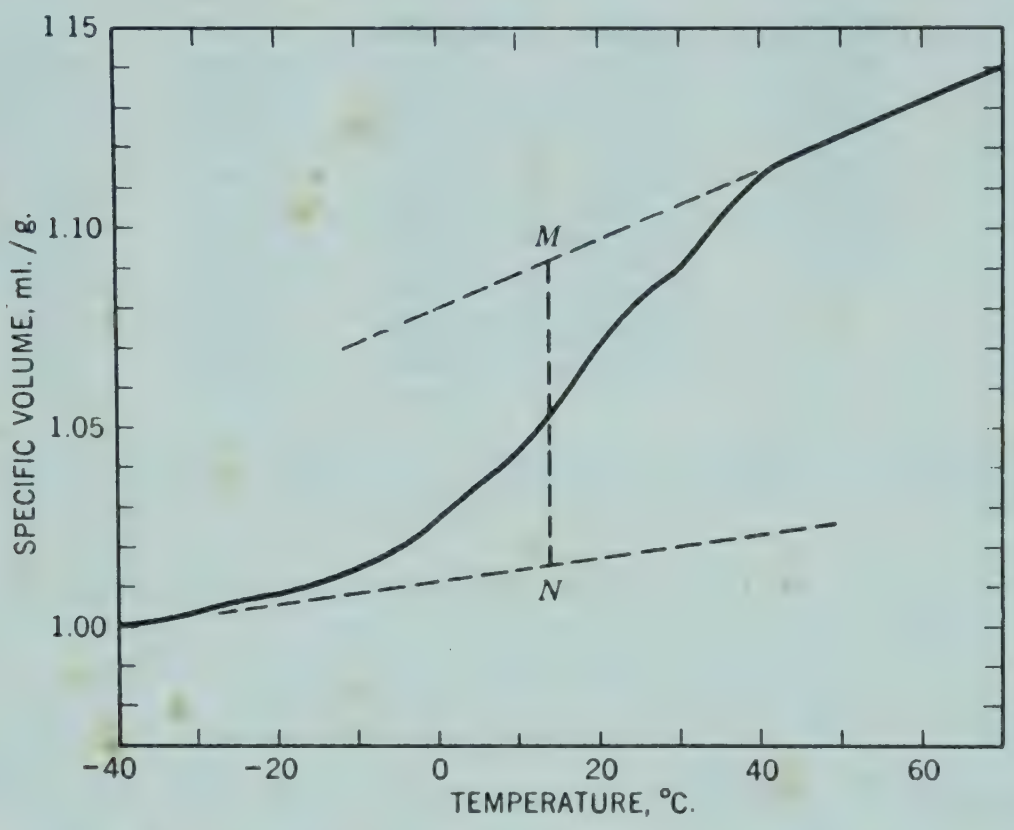


Fig. 88. Specific volume–temperature relationship of a partially hydrogenated cottonseed oil (I.V.=59.5 from data of Bailey and Singleton).[71, 80] Slanted broken lines through *M* and *N* represent prolongations of liquid and solid lines, respectively. Vertical broken line, *MN*, represents melting dilation taken at the point of half-fusion.

the preceding data applied to the oils in their most stable, highest melting forms.

The density of a partially solidified oil at any temperature is variable, according to the relative proportions of liquid and solids in the sample. A hydrogenated oil of the consistency of shortening or margarine and free of entrapped air will ordinarily have a density of about 0.92 at 20° C. or 68° F.

Magne and Skau [70] have reported data on the density at different temperatures of winterized cottonseed oil (iodine value, 110.6) mixed in various proportions with petroleum naphtha (Skellysolve B), acetone, and methyl ethyl ketone. Their figures for mixtures of the oil with petroleum naphtha are given in Table 114. Similarly detailed data for the other mixtures may be found in the original publication.

TABLE 114

Density of Mixtures of Winterized Cottonseed Oil (Iodine Value, 110.6) and Skellysolve B[a]

Per cent by weight of oil	Temperature, °C.					
	−20	−10	0	10	25	40
	Density					
0	0.7173	0.7066	0.6980	0.6908	0.6773	0.6637
11.15	0.7373	0.7294	0.7208	0.7121	0.6993	0.6859
19.22	0.7524	0.7445	0.7350	0.7276	0.7149	0.7020
29.06	0.7735	0.7659	0.7569	0.7494	0.7369	0.7245
38.98	0.7935	0.7855	0.7772	0.7693	0.7574	0.7452
49.00	0.8160	0.8087	0.8010	0.7931	0.7818	0.7697
58.28	0.8378	0.8302	0.8224	0.8149	0.8036	0.7924
71.73	—	0.8633	0.8555	0.8485	0.8374	0.8266
78.76	—	0.8813	0.8740	0.8669	0.8561	0.8455
88.00	—	0.9073	0.9004	0.8933	0.8830	0.8725
100	—	—	0.9322	0.9253	0.9151	0.9056

[a] F. C. Magne and E. L. Skau, *Ind. Eng. Chem.*, **37,** 1097–1101 (1945).

D. Properties Involving Melting and Solidification

1. Melting Point. Congeal Point. Titer

The *melting point* of cottonseed oil examined in capillary tubes is usually stated to be 5–10° C. For a typical oil with an iodine value of 108, Wakeham and Magne [69] give a melting range of −5.6° to +4.2° C. and a solidification range of −4.4° to −9.9° C.

Typical figures for the capillary tube melting point of hydrogenated cottonseed oils, as a function of iodine value, are given in Table 115.

A more certain indication of the temperatures at which melting actually begins and ends is furnished by calorimetric and dilatometric methods of examination. In a calorimeter of the proper design, the beginning of melting is detected with great delicacy and certainty by the sudden increase in the apparent specific heat of the sample as heat begins to be absorbed in the fusion of the fat. The change in volume accompanying melting furnishes a similarly exact indication of the point at which liquefaction begins or becomes complete in the dilatometer. Since dilatometric measurements are made under static rather than dynamic conditions, the final melting point represents a state approaching closely to complete equilibrium, which is a condition difficult or impossible to attain by ordinary melting point methods.

By calorimetric means, Oliver *et al.*[72] found that a sample of cottonseed oil with an iodine value of 108.3 began to melt at −75° C. An almost

[72] G. D. Oliver, W. S. Singleton, S. S. Todd, and A. E. Bailey, *Oil & Soap,* **21,** 297–300 (1944).

TABLE 115

Iodine Value and Melting Point and Titer in a Typical Series of Hydrogenated Cottonseed Oil Samples

Iodine value	Melting point, °C.[a]	Titer, °C.[b]
108.5	—	34.9
97.9	—	33.9
86.9	—	33.8
81.5	—	33.7
76.2	—	33.8
71.7	—	34.7
66.4	44.0	35.7
55.6	45.5	40.2
45.6	50.0	44.9
34.5	54.6	50.8
22.1	58.1	56.0
14.4	59.8	58.8
6.9	61.6	60.9

[a] Final melting point, as observed in samples heated slowly in closed capillary tubes.

[b] AOCS method.

completely hydrogenated sample of oil (iodine value, 0.85) began to melt at −15° C.[73] A sample of cottonseed oil examined dilatometrically by Kraemer and Bailey [74] was completely melted, only at a temperature of 11.6° C. The highly hydrogenated cottonseed oil referred to above exhibited a final melting point of 62.5° C. according to dilatometric observations,[71] as compared with 62.3° C. obtained by the ordinary capillary tube method.

The *titer,* or solidifying point of the separated fatty acids, is a useful characterizing property of oils. Owing to its relatively high content of saturated acids, cottonseed oil has a higher titer than most oils of equivalent iodine value. The usual range of titer is about 33.5–35.5°, although values as low as 32° or as high as 37° are often encountered. The titer is dependent principally upon the content of saturated fatty acids. The effect of fractional crystallization—to reduce the content of saturated acids—on the titer of cottonseed oil fatty acids, as determined by Singleton *et al.,*[75] is shown in Figure 89.

Winterization reduces the titer of cottonseed oil, *e.g.,* from about 34.5° to 33.0° C. Selective hydrogenation of cottonseed oil, in its first stages, causes a slight decrease rather than an increase in the titer. Titers of samples from a typical hydrogenation run on cottonseed oil are given in Table 115.

[73] G. D. Oliver and A. E. Bailey, *Oil & Soap,* **22,** 39–41 (1945).
[74] E. A. Kraemer and A. E. Bailey, *Oil & Soap,* **21,** 254–256 (1944).
[75] W. S. Singleton, M. Lambou, and A. E. Bailey, *Oil & Soap,* **22,** 168–174 (1945).

The *congeal point* or *setting point,* which is a solidification point determined on the fat under specified conditions, is not a useful or easily determined characteristic of unhydrogenated cottonseed oil, but is much used in controlling the hydrogenation process. Values obtained for this characteristic depend somewhat upon the method of determination; there is at present no standard method. Margarine oils and shortenings are usually hydrogenated to a congeal point of 26–32° C.

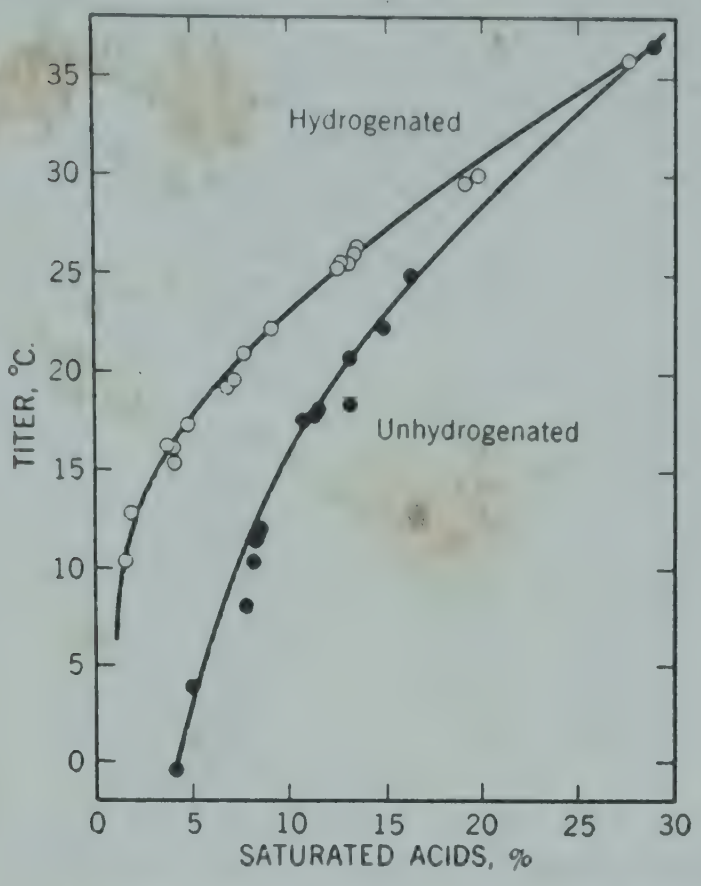


Fig. 89. Relationship between saturated acid content and titer in fractionally crystallized cottonseed oil fatty acids.[75] Iodine value of acids from unhydrogenated oil, 104.7 and 106.6, and of acids from hydrogenated oil, 69.7.

2. Cloud and Pour Points. Cold Test

The cloud point of cottonseed oil, as determined by the AOCS modification of the ASTM method usually varies from about 33° to 40° F., and the ASTM pour point varies from about 25° to 32° F. In the AOCS cold test, wherein the oil sample is immersed in ice and water at 32° F., cottonseed oil will almost invariably cloud within less than 1 hour. However, winterization of the oil ordinarily reduces the cloud point to 22–26° F. and the pour point to 18–22° F., and increases the cold test to 8–20 hours.

3. Proportions of Liquid and Solids. Consistency

The consistency of partially solidified fats is determined by the proportion of fat in the solid form and by certain other factors which probably include the size, size distribution, and rigidity of the solid crystals, and the degree to which the crystals tend to flocculate or adhere to one another.

A variety of methods are in use for measuring the consistency of plastic cottonseed oil products; some of the methods applicable to shortenings and other commercial products have been described by Rich.[76] A micropenetration method has been developed [77, 78] in which both the solidification and measurement of consistency of the sample are carried out under standardized conditions. Typical variations of micropenetration with iodine value in selectively hydrogenated cottonseed oil [78] are shown in Figure 90.

[76] A. D. Rich, *Oil & Soap,* **19,** 54–57 (1942).
[77] E. Freyer, *Ind. Eng. Chem., Anal. Ed.,* **2,** 423–424 (1930).
[78] R. O. Feuge and A. E. Bailey, *Oil & Soap,* **21,** 78–84 (1944).

Estimates of the percentages of solids and liquid at different temperatures in a raw and a hydrogenated cottonseed oil were made calorimetrically by Bailey and Oliver.[79] The unhydrogenated oil (iodine value, 108.3) was estimated to be 75% solid at −16° C., 50% solid at −10° C., and 20% solid at 0° C. Later work of Singleton and Bailey [80] showed that in the upper ranges of melting somewhat high values for per cent solids are

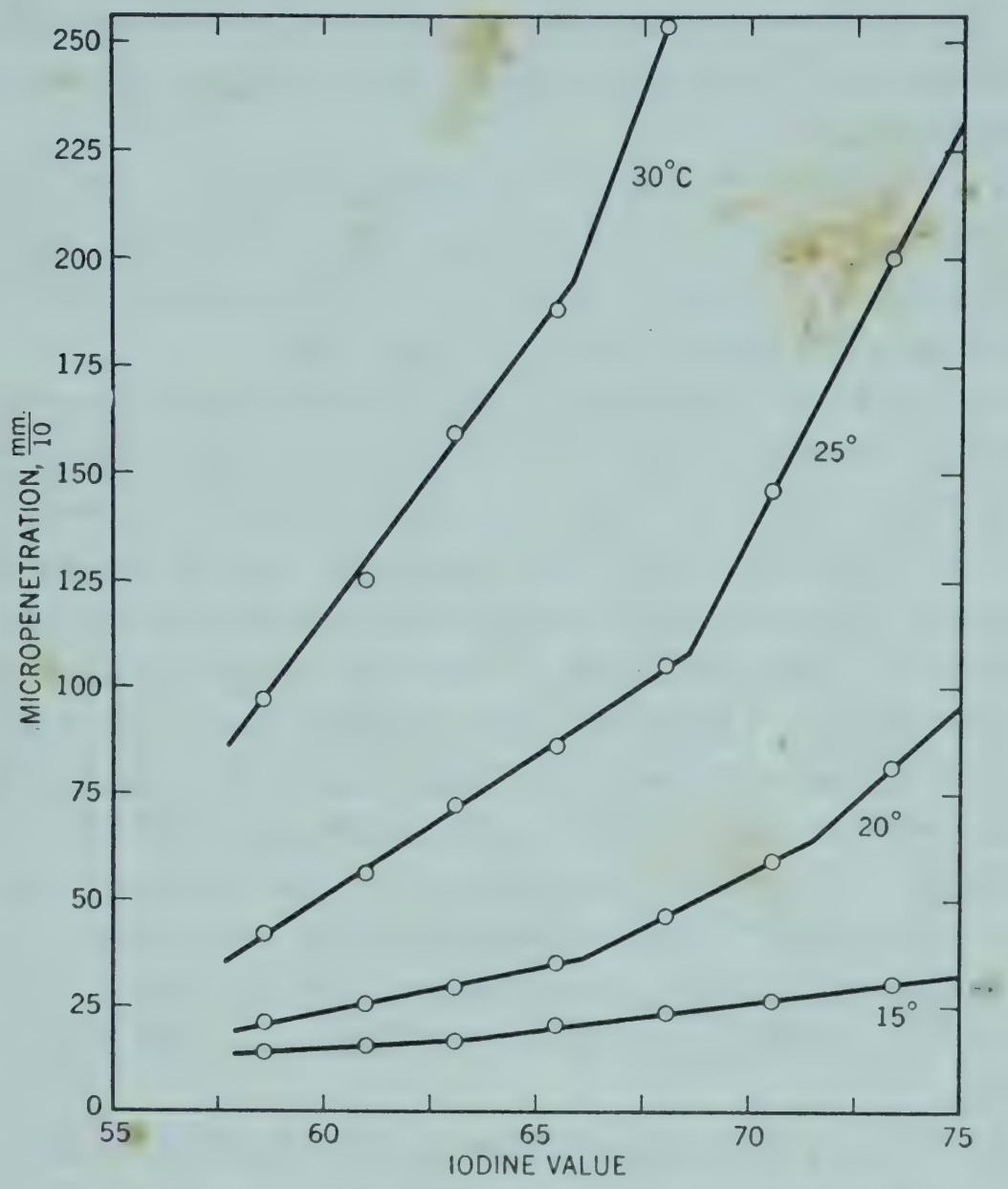


Fig. 90. Typical variation in micropenetrations of cottonseed oil with selective hydrogenation.[78]

obtained by the calorimetric technique, owing to a lack of equilibrium between solids and liquid in the calorimeter. Estimates by the more satisfactory dilatometric method on a sample of hydrogenated cottonseed oil slightly firmer than a commercial shortening (iodine value, 59.5) were: at 20° C., 33.1% solids; at 25° C., 23.7% solids; at 30° C., 19.0% solids. Apparently, an oil hydrogenated selectively to the consistency of shortening or margarine will contain about 26–28% solids at 20° C. (68° F.) and about 20–22% solids at 25° C. (77° F.). However, many commercial shortenings and margarines are blends of hard and soft stocks in which the consistency-solids content relationships are somewhat different.

[79] A. E. Bailey and G. D. Oliver, *Oil & Soap,* **21,** 300–302 (1944).
[80] W. S. Singleton and A. E. Bailey, *Oil & Soap,* **22,** 295–299 (1945).

E. Solubility and Miscibility

At ordinary temperatures, liquid cottonseed oil is miscible in all proportions with most organic solvents. However, it is immiscible with a few solvents, *e.g.*, furfural, and at low temperatures it becomes immiscible in certain intermediate proportions with certain polar solvents, such as acetone and methyl acetate. Certain hydrocarbons, such as liquid propane, which ordinarily mix freely in all proportions with cottonseed oil and other fatty oils, become but partially miscible in the region approaching their critical temperatures.[81]

At temperatures near that of solid carbon dioxide (—78° C.), cottonseed oil becomes but sparingly soluble in organic solvents. The solubility data of Singleton and Bailey [82] on raw and hydrogenated cottonseed oils in different solvents are recapitulated in Table 116.

These data are to be regarded as only approximate, since insufficient time was allowed for the attainment of complete equilibrium in the chilled solvent–oil mixture, and recovery of the dissolved oil was not quite quantitative. Nevertheless, they give a general idea of the solubility behavior of the oils. It is to be noted that a considerable part of the material soluble at very low temperatures consists of nonglyceridic substances, including tocopherols and probably also hydrocarbons, etc. For example, the soluble residue from acetone and hydrogenated oil of 59.5 iodine value, at —74° C. and at a solvent : oil ratio of 8 : 1, contained 32.1% tocopherols.

The solubility of neutral cottonseed oil in water is very slight. Parsons and Holmberg [83] have determined the solubility of water in winterized cottonseed oil to be approximately as follows: at 32° F., 0.074%; at 50° F., 0.090%; at 60° F., 0.106%; at 70° F., 0.121%; at 90° F., 0.138%.

Cottonseed oil and other fatty oils readily dissolve 4–10% of their own volume of air and other gases at ordinary temperatures. The solubility of most gases in fats, unlike the solubility of gases in water, increases with increasing temperature. According to Parsons [84] the Ostwald solubility coefficient [85] of hydrogen in raw or hydrogenated cottonseed oil increases from 0.0463 at 30.5° C. to 0.1024 at 147.8° C. In the same interval the solubility coefficient of nitrogen increases from 0.0711 to 0.1183. The solubility coefficients of other gases are: carbon monoxide, 0.1201 at 78.2° C. and 0.1470 at 147.8° C.; oxygen, 0.1450 at 67.0° C.

[81] A. W. Hixson and J. B. Bockelmann, *Trans. Am. Inst. Chem. Engrs.*, **38,** 891–930 (1942).

[82] W. S. Singleton and A. E. Bailey, *Oil & Soap,* **21,** 224–226 (1944).

[83] L. B. Parsons and C. O. Holmberg, *Oil & Soap,* **14,** 239–241 (1937).

[84] L. B. Parsons, quoted in A. E. Bailey, *Industrial Oil and Fat Products,* Interscience, New York, 1945, p. 76.

[85] The Ostwald Solubility coefficient is defined as unit volumes of gas dissolving at 760 mm. pressure in a unit volume of oil, volumes of both gas and oil being measured at the temperature in question.

TABLE 116

Approximate Solubility of Unhydrogenated and Hydrogenated Cottonseed Oils in Some Organic Solvents[a]

Solvent	Solvent : oil ratio (by wt.)	Temperature, °C.	Percentage of total oil	
			Crystallized	In solution
Raw Oil (I.V. = 103.2)				
Acetone	8 : 1	−40	73.7	26.3
Acetone	8 : 1	−60	99.06	0.94
Acetone	8 : 1	−73	99.45	0.55
Acetone	8 : 1	−90	99.53	0.47
Hydrogenated Oil (I.V. = 59.5)				
Acetone	8 : 1	15	31.2	68.8
Acetone	8 : 1	0	47.4	52.6
Acetone	8 : 1	−20	74.4	25.6
Acetone	8 : 1	−40	97.8	2.2
Acetone	8 : 1	−60	99.60	0.40
Acetone	8 : 1	−74	99.86	0.14
Acetone	8 : 1	−90	99.90	0.10
Acetone	5 : 1	−60	99.78	0.22
Acetone	20 : 1	−60	99.46	0.54
Methyl ethyl ketone	10 : 1	−60	98.8	1.2
Skellysolve B	10 : 1	−60	84.4	15.6
Hydrogenated Oil (I.V. = 0.44)				
Acetone	8 : 1	25	97.2	2.8
Acetone	8 : 1	0	98.0	2.0
Acetone	8 : 1	−20	99.19	0.81
Acetone	8 : 1	−40	99.52	0.48
Acetone	8 : 1	−60	99.69	0.31
Acetone	8 : 1	−78	99.90	0.10
Skellysolve B	6.3 : 1	−60	99.38	0.62

[a] W. S. Singleton and A. E. Bailey, *Oil & Soap*, **21**, 224–226 (1944).

and 0.1535 at 84.7° C.; carbon dioxide, 0.920 at 64.3° C. and 0.619 at 139.4° C. In all cases there is a linear increase in the solubility coefficient with increased temperature.

F. Thermal Properties

1. Heat of Combustion

The heat of combustion of either raw or hydrogenated cottonseed oil is very close to that of other fats and oils of comparable molecular weight, and may be considered to average about 9,500 calories (or 9.5 kilocalories) per gram.

2. Specific Heat

The specific heats of raw and hydrogenated cottonseed oils at relatively low temperatures, according to the data of Oliver and co-workers,[72, 73] are given in Table 117. The material referred to as "solid" in this table

TABLE 117

Specific Heat of Raw and Hydrogenated Cottonseed Oils in the Liquid and Solid States[a]

Oil	Iodine value	State	Temperature, °C.	Specific heat, cal./g.
Unhydrogenated	108.3	Liquid	19.3	0.475
			50.7	0.495
Unhydrogenated	108.3	Solid[b]	−95.7	0.276
			−57.3	0.344
Hydrogenated	59.5	Liquid	43.4	0.499
			66.9	0.513
Hydrogenated	59.5	Solid[b]	−76.9	0.288
			−41.5	0.342
Hydrogenated	0.85	Liquid	67.0	0.524
			82.0	0.537
Hydrogenated	0.85	Solid[b]	−69.8	0.270
			−17.5	0.342

[a] G. D. Oliver, W. S. Singleton, S. S. Todd, and A. E. Bailey, *Oil & Soap*, **21**, 297–300 (1944). G. D. Oliver and A. E. Bailey, *ibid.*, **22**, 39–41 (1945).

[b] Highest melting and most stable form. True specific heat of solid, including no heat of fusion.

was completely free of liquid oil in the temperature ranges recorded, hence the tabulated specific heats include no heat of fusion. Within limited ranges the specific heat both of solid and liquid varies linearly with temperature, hence values intermediate between those recorded may be estimated by simple interpolation.

Gudheim [86] has determined the amount of heat required to raise the temperature of different samples of hydrogenated cottonseed oil from 21° to 100° C. His results, in terms of calories per gram at different iodine values, were as follows: at 69.2 iodine value, 44.6 calories; at 56.5, 50.3; at 41.0, 57.6; at 24.8, 66.4; at 11.9, 75.1; at 0.5, 78.2. These values, of course, include both sensible heat and heat of fusion.

Clark, Waldeland, and Cross [86a] have reported for a highly hydrogenated cottonseed oil (I.V. = 6.5) the following values for specific heat at high temperatures (°C.): at 100.2°, 0.533; at 140.3°, 0.544; at 160.4°, 0.570; at 201.4°, 0.584; at 219.4°, 0.595; at 250.1°, 0.638. Values for soybean oil (I.V. = 128.3) were: at 100.4°, 0.508; at 120.8°, 0.527; at 141.3°, 0.531; at 161.9°, 0.550; at 182.7°, 0.567; at 200.1°, 0.594; at 219.5°, 0.581;

[86] A. R. Gudheim, *Oil & Soap*, **21**, 129–133 (1944).

[86a] P. E. Clark, C. R. Waldeland, and R. P. Cross, *Ind. Eng. Chem.*, **38**, 350–353 (1946).

at 240.2°, 0.617. The specific heats of unhydrogenated and of partially hydrogenated cottonseed oil may be taken as intermediate between the values given for highly hydrogenated cottonseed oil and soybean oil, since the specific heat of oils appears to be dependent upon their degree of unsaturation.

Oliver *et al.*[72] found, for a liquid mixture of 52.1 parts by weight of cottonseed oil (iodine value, 108.3) and 47.9 parts of Skellysolve B (petroleum naphtha), a specific heat of 0.478 at 2.9° C. and of 0.496 at 30.3° C.

In hydrogenated, plastic products made from cottonseed oil or in an unhydrogenated oil at low temperatures, the heat required to increase the temperature a given amount will comprise both latent heat of fusion and sensible heat of liquid and solids. The total heat content of a hydrogenated oil as tabulated for different temperatures by Bailey and Oliver [79] will provide a fairly accurate guide for products of the consistency of shortenings or margine fat.

3. Heat of Fusion or Crystallization

The following values have been found by Oliver *et al.*[72,73] for the heats of fusion of various cottonseed oil samples solidified in the highest melting form: unhydrogenated oil (iodine value, 108.3), 20.6 cal. per g.; partially hydrogenated oil (iodine value, 59.5), 27.4 cal. per g.; almost completely hydrogenated oil (iodine value, 0.85), 44.3 cal. per g. A value of 45.3 cal. per g. was reported by Gudheim [86] for a hydrogenated oil with an iodine value of 0.5.

4. Thermal Conductivity

Values for the thermal conductivity of cottonseed oil do not appear in the literature. However, measurements have been made upon other similar fatty oils, and these are undoubtedly applicable to cottonseed oil also, with little error.

For olive oil, Davis [87] reported thermal conductivities, cal. per sec. per sq. cm. per °C. per cm., of 0.00040 at 19° C. and 0.000385 at 71° C. These correspond to respective values of 1.16 and 1.12 BTU per hr. per sq. ft. per °F. per in. The values of Davis are in close agreement with those of other investigators [88] for olive, sesame, and castor oils.

5. Vapor Pressure. Heat of Vaporization

From data obtained during the high-temperature steam deodorization of hydrogenated cottonseed oil, the vapor pressure of the neutral oil has been estimated by Bailey [89] to be 0.04 mm. of mercury at 250° C. (482° F.).

[87] A. H. Davis, *Phil. Mag.*, **47,** 972–975 (1924).

[88] See Landolt-Börnstein, *Physikalisch-chemische Tabellen,* Springer, Berlin, 1923, Tables 271 and 271a.

[89] A. E. Bailey, *Ind. Eng. Chem.*, **33,** 404–408 (1941).

An estimate of the same order of magnitude (0.01 millimeter) has been made by Lederer [90] for the vapor pressure of peanut oil at this temperature.

According to the data of Pool and Ralston [91] on various pure fatty acids, the vapor pressure in mm. of mercury for the mixed fatty acids of cottonseed oil should be approximately as follows: at 175° C., 0.9; at 200° C., 3.8; at 225° C., 12.4; at 250° C., 32.

According to the data of Lederer,[90] the heat of vaporization of the mixed fatty acids from cottonseed oil should be about 68 cal. per g. or 122 BTU per lb. at 100 mm. pressure, or 80 cal. per g., 144 BTU per lb. at 5 mm. pressure. These values check with that reported by Mills and Daniels [92] (124 BTU per lb.) for the commercial distillation of oleic acid.

6. Heat of Mixing

Mixing of an oil with an organic solvent usually brings about a slight lowering of the temperature of the mixture, due to the absorption of heat in reducing association of the oil molecules. However, certain chlorinated solvents cause an evolution of heat when mixed with oils,[93] presumably from the formation of an oil-solvent complex.

TABLE 118

Smoke, Fire, and Flash Points of Mixtures of Cottonseed Oil and Cottonseed Oil Fatty Acids[a]

FFA content of mixture, %	Smoke point, °F.	Flash point, °F.	Fire point, °F.	FFA content of mixture, %	Smoke point, °F.	Flash point, °F.	Fire point, °F.
0.055	425	613	683	9.02	245	475	560
0.33	360	600	680	11.02	230	460	525
0.65	325	590	675	25.2	220	425	470
0.92	320	585	675	38.3	215	400	450
1.45	295	575	675	62.0	208	380	340
3.07	280	540	670	100.0	195	375	430
4.45	260	500	660	—	—	—	—

[a] D. A. Morgan, *Oil & Soap*, **19**, 193–198 (1942).

According to Skau,[94] cottonseed oil and petroleum naphtha mixed at 25° C. have a maximum negative heat of mixing of approximately 2 cal. per g. of mixture or 3.5 cal. per g. of oil, with the greatest heat effect occurring in a mixture containing about 60% by weight of oil.

[90] E. L. Lederer, *Seifensieder-Ztg.*, **57**, 67–71 (1930).
[91] W. O. Pool and A. W. Ralston, *Ind. Eng. Chem.*, **34**, 1104–1105 (1942).
[92] V. Mills and R. C. Daniels, *Ind. Eng. Chem.*, **26**, 248–250 (1934).
[93] H. F. Johnstone, I. H. Spoor, and W. H. Goss, *Ind. Eng. Chem.*, **32**, 832–835 (1940).
[94] E. L. Skau, quoted in A. E. Bailey, *Industrial Oil and Fat Products*, Interscience, New York, 1945, p. 66.

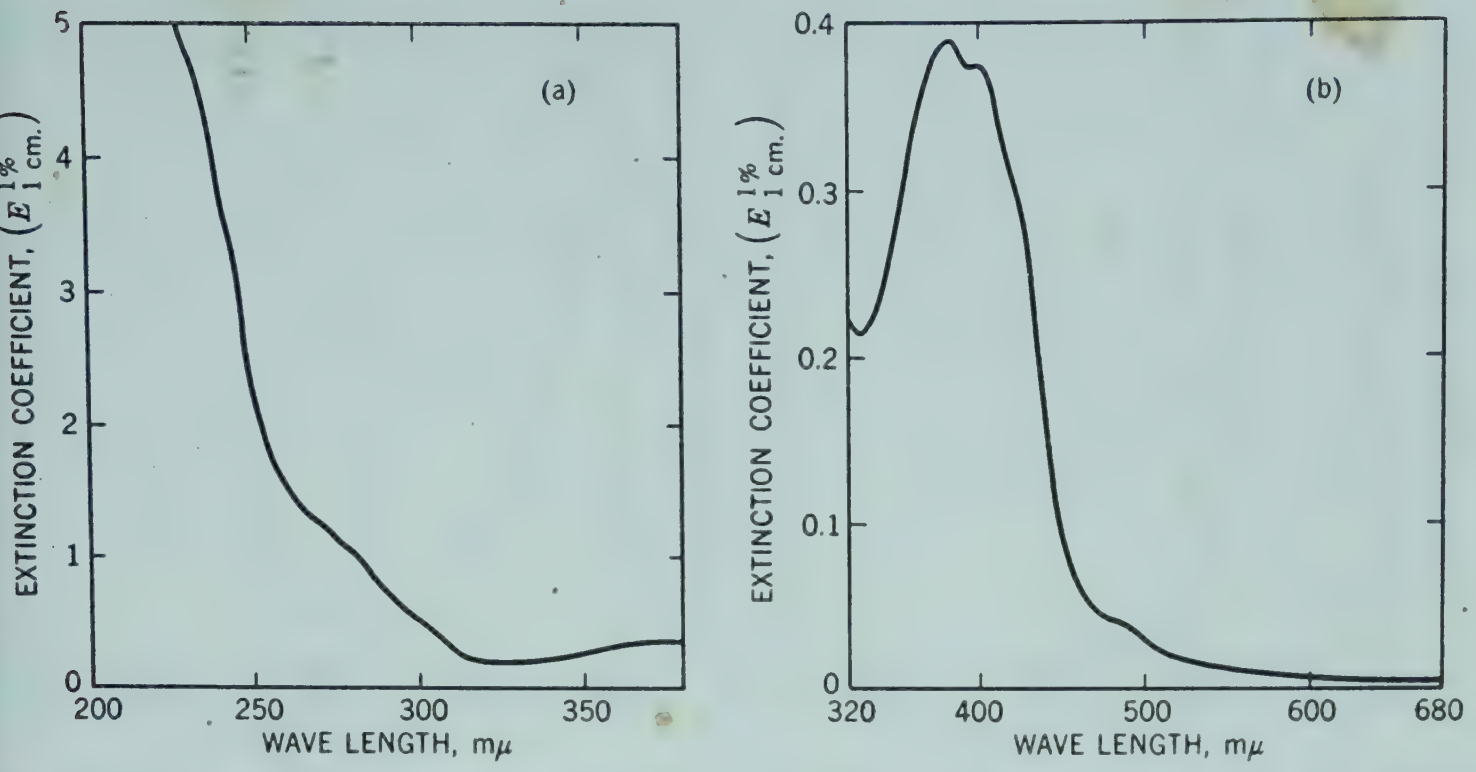


Fig. 91. Absorption spectrum of a typical crude cottonseed oil: (a) in the ultraviolet range (in iso-octane), and (b) in the visible range (in chloroform).[95]

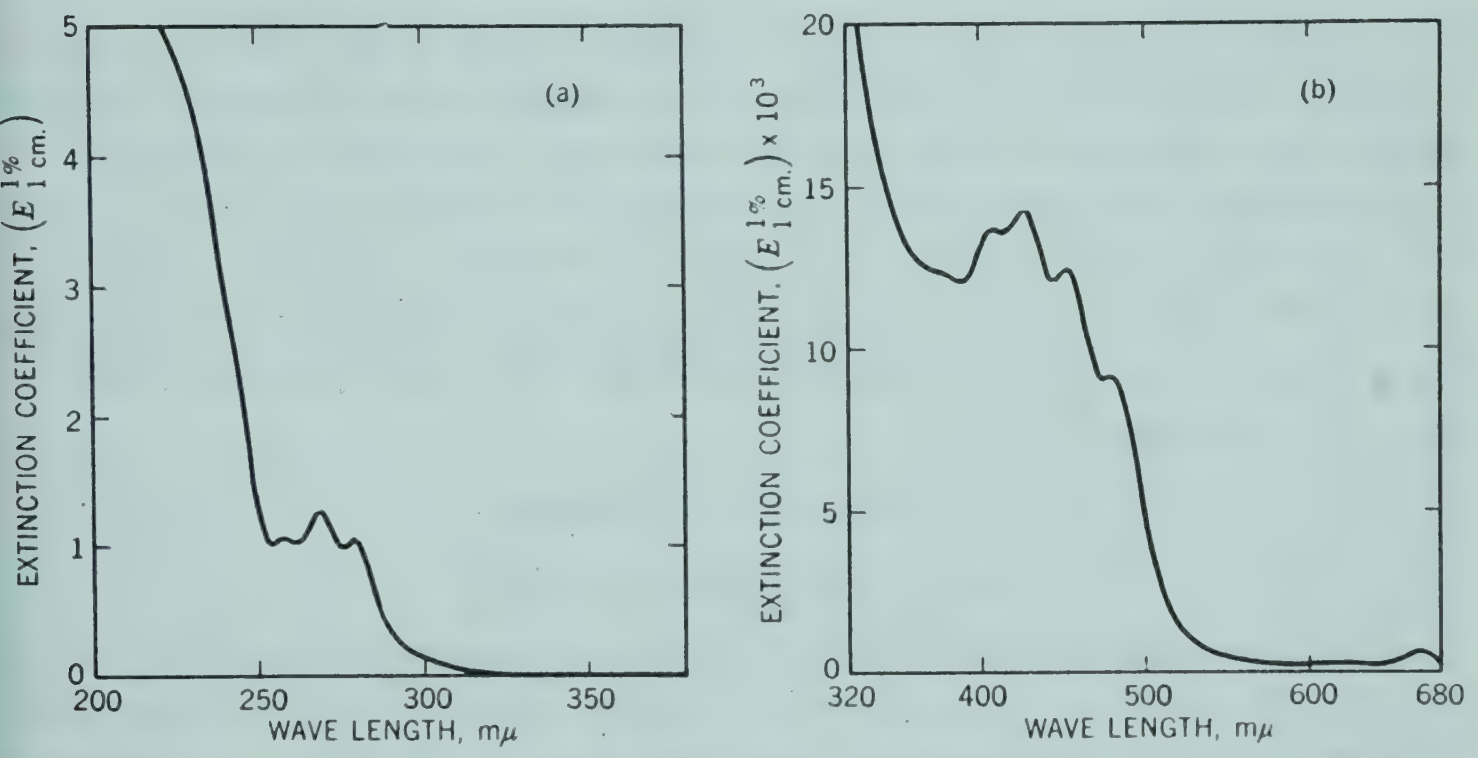


Fig. 92. Absorption spectrum of a typical refined cottonseed oil (Lovibond color, $35Y$–$6.5R$): (a) in the ultraviolet range (in iso-octane), and (b) in the visible range (in chloroform).[95]

7. Smoke, Fire, and Flash Points

The smoke, fire, and flash points of cottonseed oil and other common oils composed substantially of glycerides of C_{16} and C_{18} fatty acids are almost entirely dependent upon the free fatty acid content of the oils.

A refined oil with a free fatty acid content of 0.01–0.03% will usually

[95] Spectral curves in this section are from the data of R. T. O'Connor, obtained with a Beckmann quartz spectrophotometer, and privately communicated to the author.

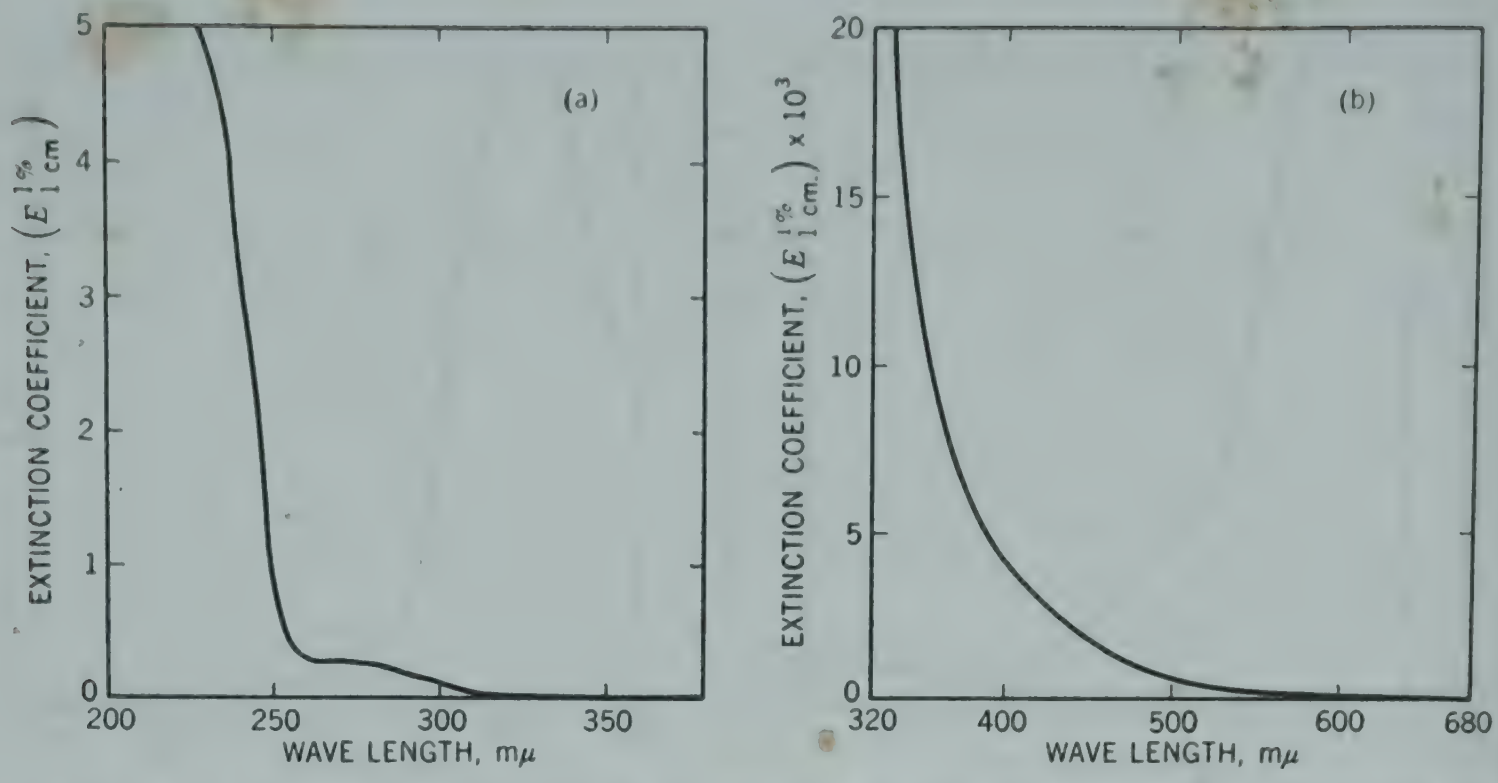


Fig. 93. Absorption spectrum of a typical refined and bleached cottonseed oil (Lovibond color, $20Y$–$2.3R$): (a) in the ultraviolet range (in iso-octane), and (b) in the visible range (in chloroform).[95]

have a smoke point of 430–450° F., a flash point of 615–625° F., and a fire point of 675–685° F.[96] An idea of the values to be expected in oils of higher free fatty acid content is furnished by the data of Morgan[96] on cottonseed oil containing various percentages of added fatty acids (Table 118). The data in this table are applicable to crude, as well as to refined oils; a crude oil with a free fatty acid content of 1.8%, for example, was found actually to have a smoke point of 293° F., a flash point of 560° F., and a fire point of 673° F.[96]

G. Optical Properties

1. Spectral Characteristics [95]

In Figures 91, 92, and 93 are reproduced spectrophotometric curves showing the spectral characteristics through both the visible and ultraviolet ranges of a single typical cottonseed oil in the crude, refined, and refined and bleached forms. In comparing the different curves it is to be noted that there are great differences in the various ordinate scales used.

The ultraviolet absorption spectra of typical samples of alkali-isomerized cottonseed oil, raw and hydrogenated to different degrees, are shown in Figure 94.

In the figures referred to above, the absorption maxima at 232 mμ are indicative of diene conjugation; those at 268 mμ are indicative of triene conjugation.[97]

[96] D. A. Morgan, *Oil & Soap*, **19**, 193–198 (1942).

[97] For information on the analysis of cottonseed oil and similar oils by ultraviolet spectroscopy, see the references cited in footnotes 14 and 15, and the review by J. P. Kass, in J. J. Mattiello, ed., *Protective and Decorative Coatings*, Vol. IV, Wiley, New York, 1944, pp. 362–405.

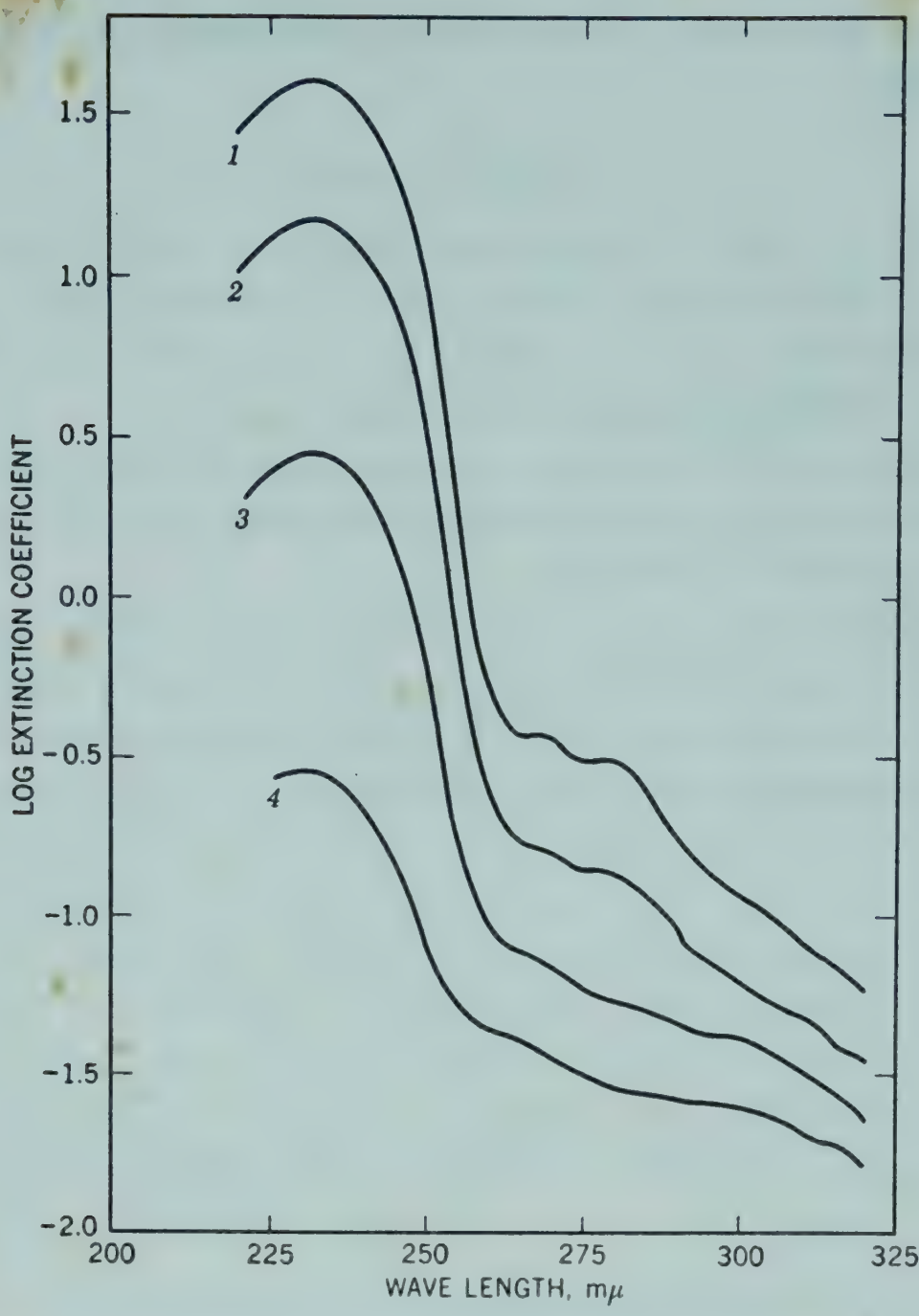


Fig. 94. Ultraviolet absorption spectra, after alkali isomerization, of raw cottonseed oil (refined and bleached) and of the same oil selectively hydrogenated to different degrees.[95] Sample *1* (raw oil): iodine value, 101.7; linoleic acid, 46.3%. Sample *2*: iodine value, 76.6; linoleic acid, 17.5%. Sample *3*: iodine value, 62.6; linoleic acid, 3.18%. Sample *4*: iodine value, 52.8; linoleic acid, 0.18%. All linoleic acid contents were calculated in terms of glycerides.

TABLE 119

Average Refractive Indices at 60°C. of Hydrogenated Cottonseed Oils of Different Iodine Values

Iodine value	Refractive index	Iodine value	Refractive index	Iodine value	Refractive index
110	1.4574	70	1.4528	30	1.4489
105	1.4570	65	1.4523	25	1.4485
100	1.4565	60	1.4518	20	1.4480
95	1.4560	55	1.4513	15	1.4476
90	1.4554	50	1.4508	10	1.4471
85	1.4548	45	1.4503	5	1.4467
80	1.4541	40	1.4498	0	1.4463
75	1.4534	35	1.4493	—	—

For further discussion of the color of cottonseed oil, see Chapter VI (pages 213–363).

2. Refractive Index

The refractive index of an average sample of cottonseed oil with an iodine value of 108, is about 1.4724 at 20° C., 1.4648 at 40° C., and 1.4572 at 60° C. A difference of 1° C. in the temperature suffices to make a difference of about 0.00038 in the refractive index.

Hydrogenation of the oil causes a progressive lowering of the refractive index. Average refractive indices for hydrogenated oils of different iodine values are recorded in Table 119.

The refractive index of unhydrogenated oils of different iodine values varies more or less as indicated in Table 119. Ordinarily, the iodine value of either a raw or hydrogenated oil may be predicted from the refractive index with an accuracy of about ± 2–3 units.

CHAPTER VIII

COTTONSEED PROTEINS

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I. Introduction

The primary purpose of this chapter is to present and discuss the chemical and physical properties of the proteins of cottonseed. Topics to be discussed include the characterization of the cottonseed proteins as to type, amino acid content, solubility phenomena, and color, and the methods of preparation for possible industrial uses. Since Chapter XXI has been devoted to a discussion of the nutritional significance of the cottonseed proteins, only occasional mention is made of this subject. Before considering the proteins of cottonseed specifically, a few general aspects of protein chemistry will be discussed.

A. General Classification of Proteins

Proteins are universally distributed and occur as integral parts of all living organisms. Chemically and basically, all proteins are made up of well-defined peptide units. Since these peptide units may be constructed of as many as twenty or more different amino acids arranged in various combinations, it is little wonder that there is such wide versatility in the chemical and physical properties of various proteins. Frequently proteins contain nonamino acid constituents which are designated as prosthetic groups. While the prosthetic groups, *e.g.*, sugars, lipids, etc., have a very pronounced effect upon the chemical, physical, and biological properties of a particular protein, they do not appreciably affect the basic structure of proteins.

On the basis of x-ray diffraction studies, all proteins may be divided into the two rather large classes: fibrous and "globular" proteins. The fibrous proteins constitute a group represented by such proteins as: keratin (wool, hair, horn) ; myosin (muscle) ; silk fibroin (silk fiber) ; and collagen (tendon, cartilage). Typical of the globular proteins are the crystalline proteins such as tobacco seed globulin, pepsin, insulin, lactoglobulin, and egg albumin.

The fibrous proteins are not truly crystalline, yet x-ray photographs exhibit well-defined patterns which resemble those obtained from simple crystalline materials. Simplest of the fibrous proteins is silk fibroin, which is considered to be made up of definite peptide units in fully extended polypeptide chains. In contrast, the fibrous protein, α-keratin, which exhibits less clearly defined x-ray diagrams than silk fibroin, is considered to consist of polypeptide chains that exist naturally in a folded state. However, the folded peptide chains of α-keratin can easily be unfolded by stretching the fiber. In the unfolded state the protein is called β-keratin. The x-ray diagram of β-keratin differs markedly from that of the unstretched α-keratin; in fact, it resembles more closely that of the fully extended protein, silk fibroin.

The truly crystalline or globular proteins, in the undenatured state, differ from the fibrous proteins in exhibiting x-ray diffraction patterns of great complexity and sharp detail, with a considerably larger number of spacings. Despite this difference, however, there appears to be a definite relationship between the globular and the fibrous proteins. For example, the treatment of crystalline egg albumin with a denaturing agent such as urea results in the loss of crystalline properties; the protein can then be drawn or spun into continuous fibers or filaments. When egg albumin fiber produced in this manner is stretched, x-ray patterns resembling those characteristic of β-keratin are obtained. It thus appears that, by suitable denaturation procedures, globular proteins can be converted to proteins which correspond closely to those of the fibrous type.

While the classification of proteins into two broad groups on the basis of x-ray patterns is adequate in some respects, it does not offer a useful basis for discussion of various proteins within either group. Since a physical chemical characterization of proteins is highly desirable, it is unfortunate that so few data are available on the vast majority of proteins. Some globular proteins, such as crystalline enzymes and blood proteins, have received considerable attention in recent years, resulting in accurate information on their amino acid content, and on the solubility, x-ray diffraction, electrophoretic, ultracentrifugal, and osmotic properties of these proteins. In the field of globular proteins of seeds, however, there are little corresponding data. For this reason, proteins which are present in seeds such as cottonseed, peanuts, soybeans, etc., must still be considered on the basis of the general classification[1] of proteins adopted by the "Committee on Protein Nomenclature." Until more precise information is available, this older classification, which is recognized as inadequate, must suffice. For the sake of brevity, only those protein types which possibly occur in

[1] "Joint Recommendations of the Physiological and Biochemical Committees on Protein Nomenclature," *J. Biol. Chem.*, **4**, xlviii (1908).

cottonseed or other seeds are included in the detailed classification given below.

1. *Simple Proteins.* Proteins which yield on hydrolysis only amino acids or their derivatives.
    a. *Albumins.* Proteins soluble in pure water and coagulable by heat.
    b. *Globulins.* Proteins insoluble in pure water, but soluble in alkalies and acids and in neutral salt solutions.
    c. *Prolamins.* Proteins soluble in 70–80% ethyl alcohol, but insoluble in water and absolute ethyl alcohol.
    d. *Glutelins.* Proteins soluble in strong alkaline solution after the removal of albumins, globulins, and prolamins.

2. *Conjugated Proteins.* Proteins united with some substance, other than as a salt, which on hydrolysis do not yield amino acids exclusively.

The conjugated proteins represent molecules which contain—in addition to the protein—certain prosthetic groups, such as carbohydrates, nucleic acid, or lipids. It should be emphasized, however, in connection with this classification, that many of the so-called simple proteins have never been prepared free of phosphorus and carbohydrate, while some of the conjugated proteins have been freed of their prosthetic groups and isolated as pure proteins.

Approximately 90% of the nitrogen in oil-free seed meals can be accounted for as either simple or conjugated proteins, whereas the nature of the remaining 10% of the total nitrogen is less clearly defined. The nature and significance of this relatively large percentage of the total meal nitrogen, which is water-soluble, has not been investigated in detail. Choline has usually been isolated from this water-soluble fraction, and it is generally supposed that amino acids, simple peptides, and peptones make up the major portion of the balance. Proteoses, which are also water-soluble and not coagulable by heat, but which are precipitated from saturated ammonium sulfate solutions, may also be present in this fraction.

B. General Industrial Application of Proteins

The fact that no two proteins from different sources have exactly the same chemical and physical properties accounts for the diverse uses of these materials and their derived products. The industrial applications of proteins may be divided into four principal groups: (*a*) those in which the size of the protein molecule remains essentially unchanged; (*b*) those in which the protein has received chemical treatment resulting in an increase in molecular size; (*c*) those in which the protein has been partially

degraded; and (*d*) those in which the protein has been completely hydrolyzed to amino acids.

It is quite difficult to make practical use of proteins without first changing their molecular size; in fact, there are few, if any, industrial globular proteins which are representative of the native protein in the original source material. However, there are times when it is desirable to maintain a protein in the least degraded state possible. For instance, in the production of artificial protein fibers from globular proteins, the success of the spinning and stretching operations depends upon altering the shape and not the size of the protein molecule. Thus, the degree of conversion of the protein molecule from its normally folded state to an elongated state (β-keratin form) will markedly affect the physical properties of the finished fiber or filament. Actually, an increase in molecular weight of the protein molecules is attained in the final protein filament because tanning agents, which not only increase the molecular weight but also cause association of the protein molecules, are used in the spinning process. Because of this action of tanning agents on proteins, the tanning process is considered perhaps the most important of the various processes employed in the industrial application of proteins. Whether tanning is accomplished by chromium- (inorganic) or aldehyde- (organic) type agents, or by a combination of both, the net result is the formation of bonds between the protein molecules, which give a product the desired resistance and rigidity. Other types of protein reactions may result in an increase in molecular weight without association between protein molecules; accordingly, products obtained by the esterification, etherification, or condensation of proteins with organic compounds have found wide application as varnishes, lacquers, and waxy materials.

By mild degradation processes, proteins—which would otherwise be useless in industry because of their viscosity and solubility characteristics—have been adapted to many uses. Although normally the seed proteins exhibit high viscosity at low concentrations, if they are subjected to mild controlled hydrolysis by acid, alkali, or enzymes, their viscosities may be lowered and stabilized. Such degraded proteins are used primarily in adhesives, paints, and various coatings and binders.

Originally, the complete hydrolysis of proteins was sought only for the identification and determination of the constituent amino acids. While this phase of protein research is still a very important one, more recently amino acids have found application in the fields of nutrition and medicine. With recognition of the nutritionally essential amino acids, there has been a better understanding of the nutritive value of various proteins. Considerable emphasis has since been placed upon the preparation of protein hydrolyzates suitable for intravenous feeding. Certain of the natural amino acids which cannot be prepared economically by organic synthesis

are prepared from protein hydrolyzates. Perhaps the most widely used amino acid obtained from protein hydrolyzates is glutamic acid. The sodium salt of this amino acid is used as a condiment, to impart a meat-like flavor to various prepared foods and sauces.

While it is not the primary purpose of this chapter to discuss the industrial application of proteins, it should be mentioned in passing that their rather wide use in paints, plastics, coatings, emulsifiers, binders, adhesives, inks, films, fibers, etc., serves to indicate the many possible applications for any new protein.

II. Isolation of Cottonseed Protein Fractions

Protein fractions designated as globulin, α-globulin, β-globulin, pentose protein, glutelin, phosphoproteins, and allergens have been isolated from the cottonseed. None of these fractions, however, has been obtained sufficiently free of contaminants to permit crystallization. While crystallization does not necessarily indicate high purity, it does indicate the removal of the major contaminants; accordingly, it is of interest to note that globulins of other dicotyledonous seeds, such as hempseed, tobacco seed, and cucumber seed, have been crystallized. Likewise, other methods for establishing the purity and number of components present in any protein fraction, such as solubility measurements, ultracentrifugation, and electrophoresis, have not been applied successfully to the cottonseed protein fractions. For the most part, these and other analytical methods which are taken for granted today were not available to the earlier workers in the vegetable protein field; but then too, in general, the oil seed proteins do not lend themselves readily to such procedures because of their insolubility in low-ionic-strength solutions and at the low temperatures generally used in solubility and electrophoretic procedures. The proteins of the cottonseed must, therefore, be considered in the light of the meager knowledge obtained by the older classical methods of protein characterization based on water, salt, alcohol, and alkali solubilities. Under such a system, the classification of proteins can only represent, at best, a crude separation into principal categories (*i.e.*, molecular weight groups), since each protein fraction thus far isolated from cottonseed probably represents two or more components.

The isolation from cottonseed of protein fractions having distinctive characteristics necessitates the use of a meal prepared under mild processing conditions. Hence, hydraulic- and expeller-pressed cottonseed meals, which have been subjected to high temperatures during their preparation, are not suitable for most fundamental research purposes. Cottonseed meal suitable for protein characterization, however, may be prepared by extracting the oil from ground or flaked cottonseed with solvents, such as benzene, ethyl ether or petroleum naphtha, at temperatures not appre-

ciably higher than 25° C. Accordingly, cottonseed meal produced by the solvent extraction of ground or flaked seeds will be referred to in this chapter as *solvent-extracted meal,* whereas *commercial meal* will refer to that produced by either hydraulic- or expeller-press methods.

A. Major Cottonseed Protein Fractions

As early as 1881, Ritthausen [2] prepared a protein fraction from cottonseed by dialyzing a sodium chloride extract of cottonseed meal. It was not until the classical investigations of Osborne and Voorhees,[3] however, that several types of nitrogenous constituents were clearly demonstrated in the cottonseed. These workers were able to show that cottonseed meal contained a globulin fraction, a proteose fraction, and an alkali-soluble fraction. Nine preparations of globulin were prepared and purified, which on elementary analysis gave such closely agreeing results that it was concluded that there was only one globulin present in the cottonseed. Although this conclusion was later shown to be incorrect, it is of considerable interest to note that these cottonseed globulin preparations were reported to contain the highest percentage of nitrogen of any major protein fraction thus far isolated from the cottonseed (*i.e.*, N, 18.64%; C, 51.71%; H, 6.86%; S, 0.62%; O, 22.17%).

α-Globulin, β-Globulin, Glutelin, and Pentose Protein Fractions

An extensive investigation of the multiple protein components of the cottonseed was first made by Jones and Csonka.[4] Using solvent-extracted cottonseed meal, they determined the solubility of the nitrogenous constituents in various solvents by successive exhaustive extractions: first with 10% sodium chloride solution, then with 70% ethanol, and finally with 0.5% sodium hydroxide solution. Since 70% ethanol failed to extract

TABLE 120

Nitrogen Extracted from Solvent-Extracted Cottonseed Meal by Various Solvents[a]

Nitrogen	Nitrogen extracted, per cent of total N
Salt-soluble protein N	76.6
Alkali-soluble protein N	8.2
Salt- and alkali-extractable nonprotein N	10.1
Residual N (by difference)	5.1

[a] D. B. Jones and F. A. Csonka, *J. Biol. Chem.*, **64,** 673–683 (1925).

[2] H. Ritthausen, *J. prakt. Chem.*, **23,** 481–486 (1881).
[3] T. B. Osborne and C. G. Voorhees, *J. Am. Chem. Soc.*, **16,** 778–785 (1894).
[4] D. B. Jones and F. A. Csonka, *J. Biol. Chem.*, **64,** 673–683 (1925).

any protein nitrogen, the absence of a prolamin-type protein in cottonseed was established. From the data presented in Table 120, it is evident that 86.7% of the total meal nitrogen is extractable by 10% sodium chloride solution, and an additional 8.2%, by 0.5% sodium hydroxide solution. The nonprotein nitrogen present in the sodium chloride extract, however, amounted to 10.1% of the total meal nitrogen, when determined by the use of tungstic acid as a protein precipitant.

Since the greater part of the nitrogenous constituents of solvent-

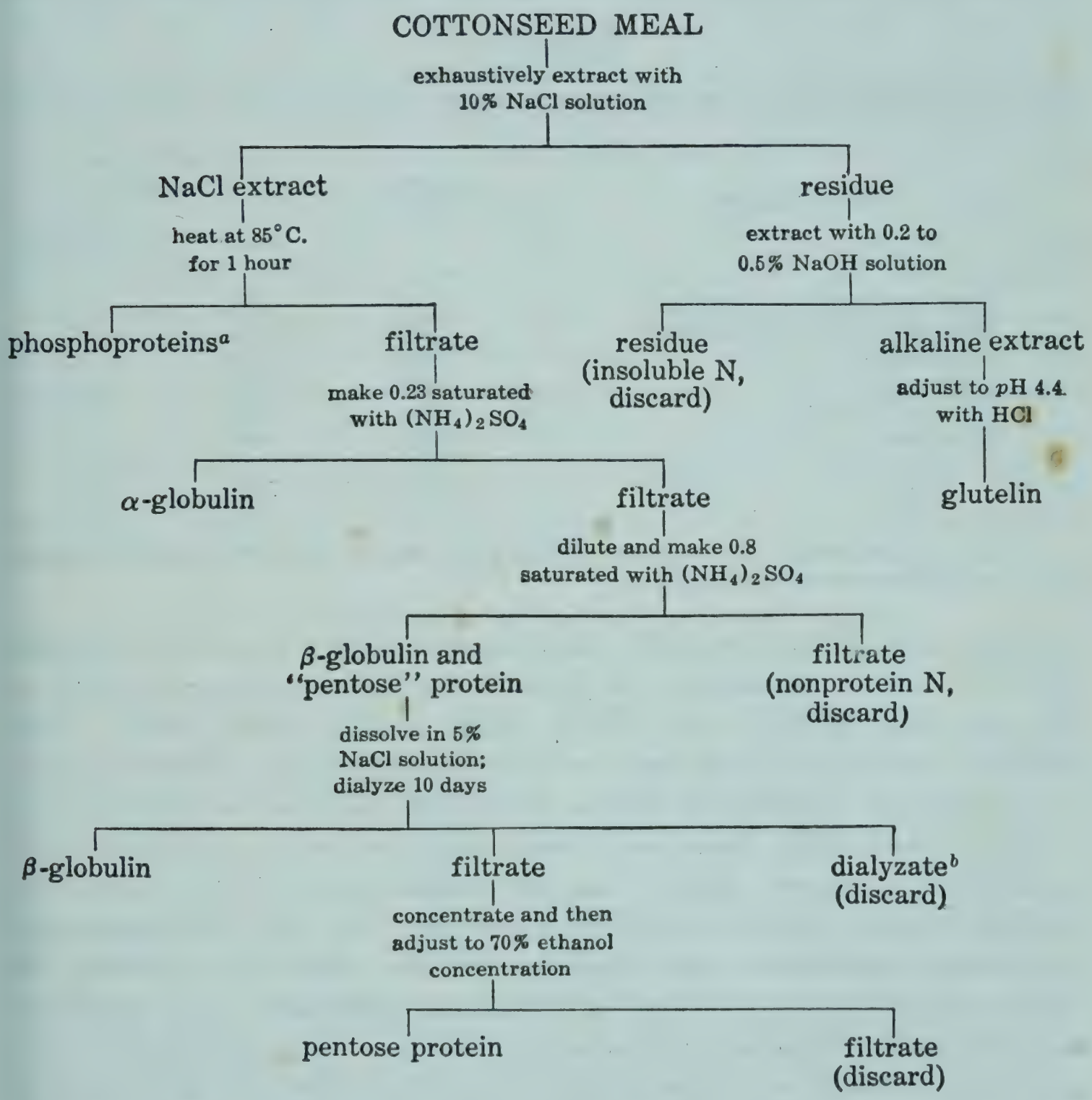


Fig. 95. Procedure for isolation of protein fractions from solvent-extracted cottonseed meal.[4]

[a] The phosphoproteins are probably impure phytin (see footnote 5).

[b] In the scheme above, the dialyzate indicates the solution on the outside of the dialyzing membrane, whereas Jones and Csonka [4] referred to the dialyzate as the solution remaining inside the membrane. Since their publication the meaning of dialyzate has changed. Their "dialysate" corresponds to the filtrate in the above scheme, which in turn means the supernatant liquid from which the β-globulin has been precipitated by dialysis.

extracted cottonseed meal is extractable by 10% sodium chloride solution, Jones and Csonka used such an extract to investigate further the number of protein components in the cottonseed. The schematic isolation procedure generally used by Jones and Csonka is presented in Figure 95.

Preliminary experiments had shown that one heat-coagulable fraction, *I*, could be obtained from the sodium chloride extract at 62° C., and another fraction, *II*, at 85° C. Fractions *I* and *II*, on a moisture-free basis, had very high ash and very low nitrogen contents: 68.2 and 67.52% ash, and 1.71 and 2.3% nitrogen, respectively (Table 121). This, according to Jones and

TABLE 121

Protein Fractions Isolated per 100 Grams of Solvent-Extracted Cottonseed Meal[a]

Fraction isolated	Quantity isolated, g.	Nitrogen in the preparation	
		Grams	% of total N
High ash-yielding Fraction *I*	0.83	0.01	0.1
High ash-yielding Fraction *II*	2.54	0.05	0.5
α-Globulin	2.59	0.43	4.9
β-Globulin	16.00	2.61	30.0
Pentose protein	2.08	0.22	2.6
Glutelin	0.73	0.09	1.0
Total	24.77	3.41	39.1

[a] D. B. Jones and F. A. Csonka, *J. Biol. Chem.*, **64**, 673–683 (1925). All the figures are calculated on air-dried materials.

Csonka, rules out the possibility that cottonseed may contain an albumin protein fraction. Instead, on the basis of the high phosphorus content of the ash (P_2O_5, 57.29%; CaO, 9.71%; MgO, 16.62%; Na_2O, 19.9%), they propose that the high-ash fractions are phosphoproteins. However, more recent work by Fontaine *et al.*[5] has shown that the phosphorus-containing fractions isolated by Jones and Csonka may be perhaps more correctly considered as impure phytin than as phosphoproteins. By heating the sodium chloride extract at 85° C. for one hour (Fig. 95), the phosphorus-containing compounds were coagulated and thus removed. In general, the subjection of protein solutions to such a heat treatment is not conducive to sufficiently precise separation of protein for analytical purposes.

From the relatively phosphorus-free extract, fractions designated as α-globulin, β-globulin, and pentose protein are obtained. Yields of the protein fractions, α-globulin, β-globulin, and pentose protein, isolated from cottonseed meal by the general scheme outlined in Figure 95, are given in Table 121. Yields of Fractions *I* and *II* and of glutelin, also given in the table, were obtained in separate experiments. Less than 40% of the total

[5] T. D. Fontaine, W. A. Pons, Jr., and G. W. Irving, Jr., *J. Biol. Chem.*, **164**, 487–507 (1946).

meal nitrogen is accounted for by the isolated fractions, the major fraction being β-globulin. Although 60% of the total meal nitrogen remains unaccounted for, as isolated fractions, Jones and Csonka were confronted with an apparently unaccountable loss in nitrogen amounting to 20% of the total meal nitrogen. It appears, however, that the apparent loss of nitrogen can be explained in the following manner. Yields of α-globulin, β-globulin, and pentose protein fractions (Table 121) were obtained from a sodium chloride extract of cottonseed meal containing *only 68%* of the total meal nitrogen, whereas Jones and Csonka had shown previously that 86.7% could be extracted (Table 120). The difference in the nitrogen content of these two extracts does, in effect, account for the apparent loss of nitrogen. It is logical to assume that, had the meal been exhaustively extracted, approximately 55 g. of protein would have been obtained in the α- and β-globulin fractions. Since the pentose protein fraction would have been completely soluble under both extraction conditions, no appreciable change in yield would be expected. Glutelin (Table 121) was obtained from cottonseed meal from which 86.7% of the total meal nitrogen had been removed by exhaustive extraction with 10% sodium chloride solution. Even so, the actual yield of the glutelin fraction is much less than would have been expected on the basis of the results presented in Table 120.

Analyses of the several protein fractions obtained by Jones and Csonka are given in Table 122. The α- and β-globulins were obtained free of

TABLE 122

Elementary Composition of Isolated Cottonseed Proteins[a]

Component	Per cent by weight			
	α-Globulin	β-Globulin	Pentose protein	Glutelin
Carbon	52.70	50.33	49.38	52.4
Hydrogen	7.58	6.65	6.27	6.27
Nitrogen	18.22	17.77	12.64	15.28
Sulfur	0.93	0.78	—	—
Phosphorus	—	—	0.194	0.35
Pentose	None	None	16.57	—
Ash	0.373	0.248	4.60	7.35

[a] D. B. Jones and F. A. Csonka, *J. Biol. Chem.*, **64**, 673–683 (1925). Figures representing the elementary composition of the proteins were calculated on the basis of the ash- and moisture-free material, with the exception of those for phosphorus and ash, which were calculated on a moisture-free basis.

carbohydrate, whereas the pentose protein, when analyzed by Tollen's phloroglucinol method, yielded 16.57% pentose. The sulfur content of the α- and β-globulins is appreciably higher than that obtained by Osborne and Voorhees[3] on their whole globulin preparations, but the nitrogen content is lower. Even after purification, the ash contents of the pentose protein and glutelin fractions are relatively high.

The work of Jones and Csonka [4] represents the only concerted effort made thus far to differentiate between the nitrogenous constituents of the cottonseed. While their work represents an excellent start, much of it needs to be repeated and expanded in the light of more recent developments in protein chemistry.

B. Cottonseed Allergens [5a]

In recent years a most comprehensive investigation of the allergenic substances in solvent-extracted cottonseed meal has been made by Spies and associates.[6-13] It was the primary purpose of this group to determine the different types of allergens present in the cottonseed, and, wherever possible, to isolate and to characterize them. Their work also serves to indicate the complexity of the problems associated with the characterization of the multiple protein components of the cottonseed.

Protein fractions, including "phosphoprotein," α-globulin, mixed α- and β-globulins, glutelin, and pentose protein, were obtained by Spies, Bernton, and Stevens [6] and were tested for allergenic activity. With the exception of the pentose protein, all of these fractions were isolated according to the procedure of Jones and Csonka.[4] Each of these protein fractions initially showed marked clinical activity, and it was only after repeated purification that it was possible to demonstrate differences between them. The protein fractions, excepting the pentose protein fraction, were freed eventually of significant clinical activity.

1. Water-Soluble Allergens

Although the water-soluble allergenic fractions may constitute as little as 1% of the oil-free meal, they are of some importance from the standpoint of the handling and of the use of cottonseed meal, edible cottonseed flour, and cottonseed oil. A schematic representation of the isolation of the water-soluble allergenic protein fractions from solvent-extracted

[5a] For immunological and clinical studies on cottonseed allergens, see E. J. Coulson, J. R. Spies, and H. Stevens, *J. Immunol.*, **41,** 375–381 (1941); *ibid.*, **46,** 347–365 (1943); *J. Allergy,* **16,** 176–183 (1945); E. J. Coulson and J. R. Spies, *J. Immunol.*, **46,** 367–376 (1943); *ibid.*, **46,** 377–389 (1945); *ibid.*, **47,** 443–452 (1943); and H. S. Bernton, J. R. Spies, and H. Stevens, *J. Allergy,* **13,** 289–295 (1942).

[6] J. R. Spies, H. S. Bernton, and H. Stevens, *J. Allergy,* **10,** 113–129 (1939).

[6a] J. R. Spies, *private communication* (1946).

[7] J. R. Spies, E. J. Coulson, H. S. Bernton, and H. Stevens, *J. Am. Chem. Soc.*, **62,** 1420–1423 (1940).

[8] J. R. Spies, H. S. Bernton, and H. Stevens, *J. Am. Chem. Soc.*, **62,** 2793–2799 (1940).

[9] J. R. Spies, H. S. Bernton, and H. Stevens, *J. Am. Chem. Soc.*, **63,** 2163–2169 (1941).

[10] J. R. Spies and E. J. Umberger, *J. Am. Chem. Soc.*, **64,** 1889–1891 (1942).

[11] J. R. Spies and E. J. Coulson, *J. Am. Chem. Soc.*, **65,** 1720–1725 (1943).

[12] H. S. Bernton, J. R. Spies, and H. Stevens, *J. Allergy,* **11,** 138–146 (1940).

[13] J. R. Spies, D. C. Chambers, H. S. Bernton, and H. Stevens, *J. Allergy,* **14,** 7–18 (1942).

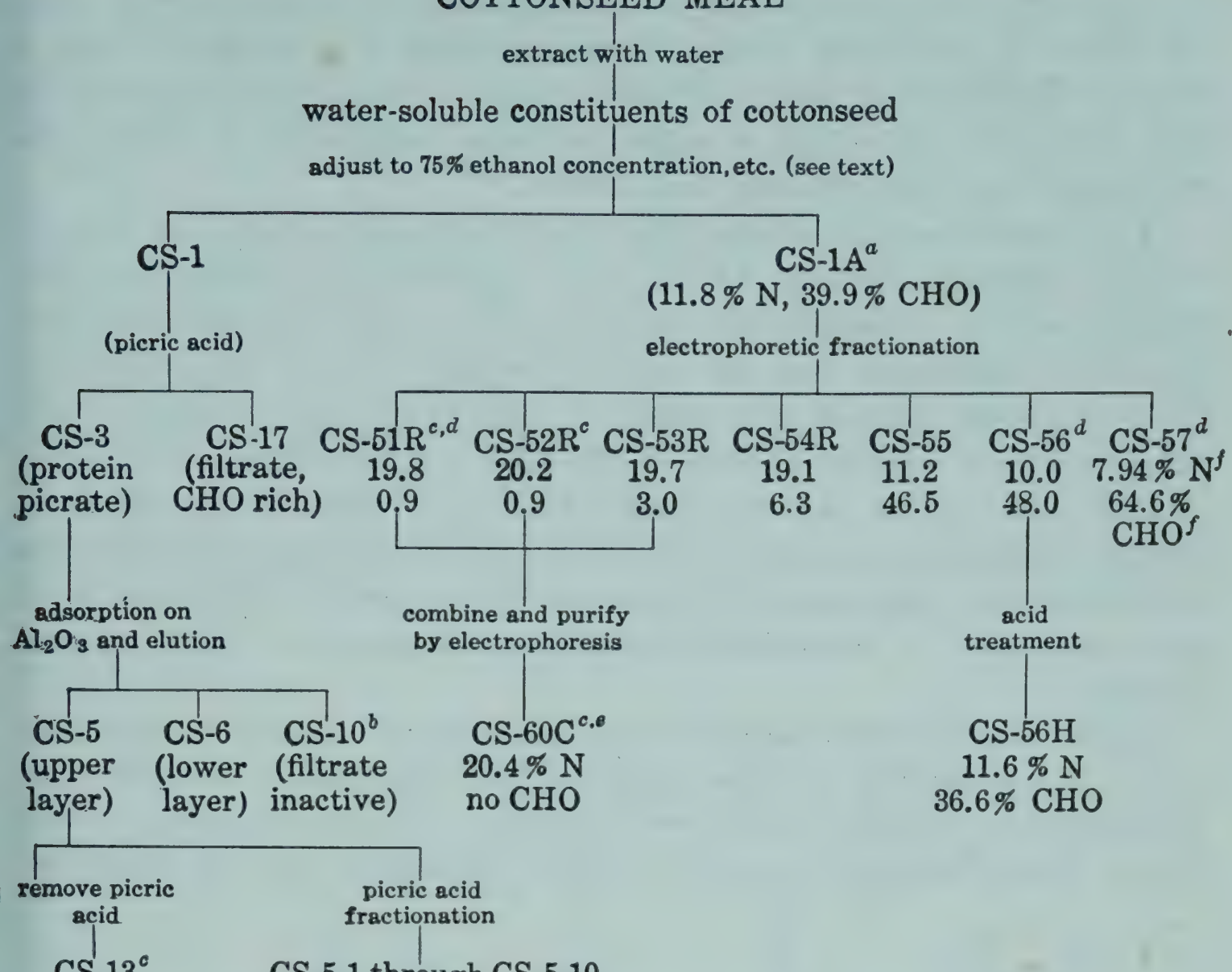


Fig. 96. Procedure for isolation of water-soluble allergenic protein fractions from solvent-extracted cottonseed meal.[7-10]

[a] CS-1 and CS-1A have equivalent allergenic and antigenic properties. Hydrogen sulfide was used in the purification before CS-1 was obtained but no hydrogen sulfide was used in preparing CS-1A. CS-1 contained approximately 15% nitrogen.

[b] All fractions are clinically active except CS-10.

[c] CS-13, CS-51R, CS-52R, and CS-60C correspond very closely in their composition and properties.

[d] CS-51R was isolated from the cathode cell, and CS-56 from the anode cell. Intermediate flasks in the electrophoretic setup are designated 1−, 2−, 2+, 1+. CS-57 represents insoluble material in flasks 1+ and 2+.

[e] CS-60C was isolated from the cathode cell and represents the most purified fraction.

[f] N = nitrogen; CHO = carbohydrate.

cottonseed meal is shown in Figure 96. The original investigation was begun with the preparation of the fraction designated as CS-1 from the water extract of cottonseed meal by the following series of steps: (*a*) boiling of the water extract to remove heat-coagulable material; (*b*) concentration of the extract to one-half its original volume; (*c*) addition of ethanol to a final volume concentration of 75%, thus causing precipitation of the allergen fraction; (*d*) dissolving of the precipitate and treatment with basic lead acetate, resulting in the removal of impurities; (*e*) removal of the excess lead with hydrogen sulfide; and (*f*) addition of ethanol to

75% concentration, resulting in the precipitation of Fraction CS-1, which was dried. In later work it was deemed desirable to eliminate the use of hydrogen sulfide from this procedure in order to measure accurately the true sulfur content of the allergen fractions designated as CS-1A and subsequent fractions obtained from CS-1A.

The properties of Fractions CS-1 and CS-1A can be listed as follows: average nitrogen content, 12 to 15%; insoluble in organic solvents; Molisch test for carbohydrates, positive, but no reduction obtained with Benedict's qualitative test for reducing sugars; positive Benedict's and Bial's (pentose) tests on a hydrochloric acid hydrolyzate; stable to high temperatures in solution (1 hour at 125–130° C.); precipitable by trichloroacetic acid; active part dialyzable, leaving a carbohydrate-rich fraction in the membrane; major active principle precipitable away from the carbohydrate by picric acid. On the basis of these results, CS-1 and CS-1A were considered to be polysaccharidic proteins and were called natural proteoses.

Spies [6a] explains that the term "natural proteose" is used because these native, water-soluble, low molecular weight components resemble proteoses in many chemical properties, but differ from the proteoses in their highly anaphylactogenic capacity. Similar substances, not yet described,

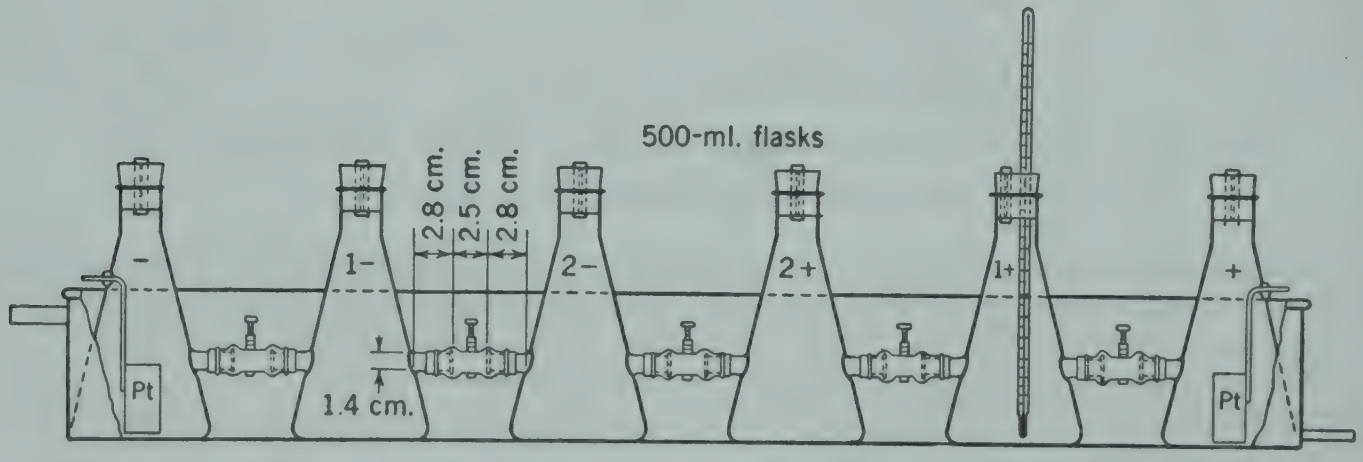


Fig. 97. Electrophoresis apparatus of Spies, Bernton, and Stevens.[9]

have been obtained from other oil-bearing seeds.[6a] As Spies points out, the natural proteoses have been largely overlooked by protein chemists in the past, but these substances deserve recognition as a well-defined class of native proteins.

Fractionation of the picrate of CS-1 was accomplished by chromatography,[7, 8] but the resulting fractions, CS-5 and CS-6, showed no appreciable differences in clinical activity, and were found to be immunologically identical with antigen present in the unheated aqueous extract of cottonseed embyro. Fraction CS-13 (picric acid-free CS-5) exhibited greater allergenic activity than CS-5, but was also immunologically identified with antigen present in the unheated aqueous extract of cottonseed embyro. The allergenic activity of CS-13A (prepared from CS-1A by

electrophoretic separation, followed by picric acid precipitation and subsequent removal of the picric acid) and CS-13 were analogous. Fractions CS-13 and CS-13A gave the usual protein tests and a positive Molisch test, but the amount of carbohydrate was so small that even after hydrolysis there were insufficient reducing sugars present to reduce Benedict's reagent. Fraction CS-13A showed the following percentage composition: C, 43.4; H, 6.78; N, 18.1; S, 2.04, 2.09; P, negative, H_2O, 9.5; ash, 0.51.

Fraction CS-1A, when subjected to high voltage electrophoresis [9] in the apparatus shown in Figure 97, was qualitatively separated into the several fractions shown in Table 123 and Figure 96. It is important to note,

TABLE 123

Chemical Properties of Fractions Obtained in an Electrophoretic Fractionation of 400 Grams of a Cottonseed Allergenic Fraction, and of Subfractions Obtained by Chemical Procedures[a]

Fraction	Yield, g.	Total N content, %	Proportion of total N pptd. by 5% trichloroacetic acid, %	Carbohydrate content, %	Amino N content, %	Total S content, %	Cystine content, %[e]	
							Found	Calcd.
CS-1A*	—	11.8	74.8	39.9	0.36	—	—	—
CS-51R(−)[b]	9.2	19.8	91.0	0.9	0.53	2.29	7.60	8.58
CS-52R(1−)[b]	8.8	20.2	89.7	0.9	—	2.24	8.45	8.40
CS-53R(2−)[b]	7.1	19.7	84.6	3.0	—	2.04	—	—
CS-54R(2+)[b]	3.5	19.1	81.5	6.3	—	1.96	—	—
CS-55(1+)[c]	22.6	11.2	69.6	46.5	—	—	—	—
CS-56(+)[c]	84.5	10.0	69.8	48.0	0.51	2.37	3.24	8.88
CS-57(1+, 2+)[c]	79.7	7.94	—	64.6	—	0.98	—	—
CS-56H[d]	—	11.6	65.1	36.6	0.52	2.04	4.21	7.64

* Starting material.

[a] J. R. Spies, H. S. Bernton, and H. Stevens, *J. Am. Chem. Soc.*, **63,** 2163–2169 (1941). Allergenic fraction referred to is their CS-1A.

[b] CS-51R, CS-52R, and CS-54R were isolated from the designated cells, but only after precipitating as the picrate and subsequently freeing the fraction of picric acid.

[c] CS-55, CS-56, and CS-57 were isolated from the designated cells and were not purified by picric acid precipitation.

[d] CS-56H was obtained after refluxing CS-56 with 0.1 *N* H_2SO_4 for four hours.

[e] No methionine was found.

however, that it was necessary to precipitate the protein from the cathode cells with picric acid in order to obtain Fractions CS-51R, CS-52R, CS-53R, and CS-54R in as high degree of purity as shown. A similar picric acid precipitation technique was not employed in obtaining CS-55, CS-56, and CS-57, which made these latter fractions comparatively higher in carbohydrate content than the preceding ones. Fraction CS-56 was later treated with picric acid, but a protein fraction was thus obtained which contained only 13% nitrogen.

All fractions listed in Table 123 had allergenic activity and, the lower the carbohydrate content, the higher the clinical activity. Certain perti-

nent facts were established as a result of this work on the allergenic fractions, which may be listed as follows: (*a*) the polysaccharide was chemically attached to the protein; (*b*) the polysaccharide influenced the acidity or basicity of the fractions, which accounted for their migration; and (*c*) CS-56, when boiled with 0.1 *N* sulfuric acid, was split into reducing pentoses and an active polysaccharide-protein, CS-56H, which contained 36.6% nonreducing carbohydrates.

From a chemical standpoint, the fractions listed in Table 123 are of particular interest because of their high sulfur content and because an absence of methionine is reported. While all of the sulfur of CS-51R and CS-52R is accounted for by cystine, only approximately one-half of the sulfur of the high-carbohydrate fractions, CS-56 and CS-56H, occurs in this form. The remainder of the sulfur in the latter fractions presumably occurs in a form other than methionine or cystine. Perhaps it is of some significance that on an equivalent nitrogen basis the high-carbohydrate fractions, CS-56 and CS-56H, contain about 4.5 and 4.0% sulfur, respectively, and approximately twice as much amino nitrogen as CS-51R. The possibility that the sulfur may exist in a form other than as in a known amino acid is suggested by these results, but consideration should also be given to the fact that the high carbohydrate content of the CS-56 and CS-56H fractions might have influenced the determination of cystine as well as the detection of methionine.

A carbohydrate-free allergenic fraction, CS-60C, was prepared by subjecting a mixture of CS-51R, CS-52R, and CS-53R to repeated high-voltage electrophoresis in an unbuffered solution.[10] The chemical composition of CS-60C, expressed on an ash- and water-free basis, was as follows:

Nitrogen	20.4%
Carbon	48.2%
Hydrogen	6.58%
Sulfur	2.35%
Nitrogen pptd. by 5% trichloroacetic acid (20° ± 0.1° C.)	86.6%
$[\alpha]_D^{20}$ (1% water solution)	−140
$[\alpha]_D^{20}$ (2% water solution)	−135

Fraction CS-60C was further characterized by determining the ultraviolet absorption curve of a 0.413% water solution as shown in Figure 98. The absorption maximum at 2700–2800 Å. was initially interpreted as indicating that CS-60C contained tyrosine but no tryptophan; later work[11] showed the presence of an appreciable amount of tryptophan, however. Phenylalanine, which has an absorption maximum at approximately 2575 Å., is either absent in this fraction or occurs in too small an amount to be detected in the presence of tyrosine and tryptophan.

Precise solubility measurements at *p*H 5.0 on CS-60C and CS-51R failed to demonstrate homogeneity in these fractions. Instead, the solubility curves shown in Figure 99 are similar to those obtained for solid solutions. Fraction CS-60C probably represents a mixture of active proteins whose structural variations are too slight

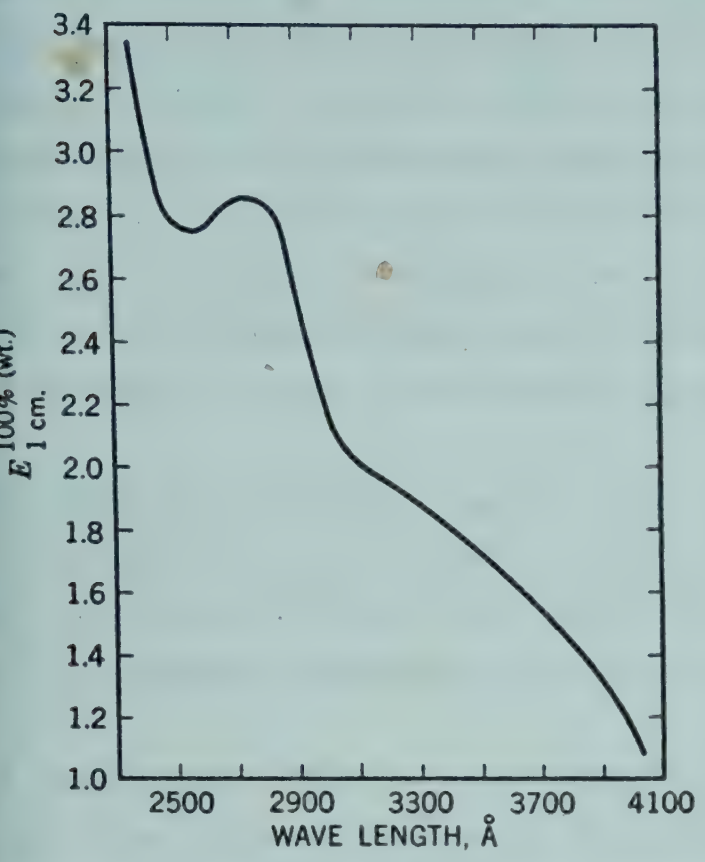


Fig. 98. Ultraviolet absorption curve of a carbohydrate-free, water-soluble allergenic fraction (CS-60C) from cottonseed meal.[10]

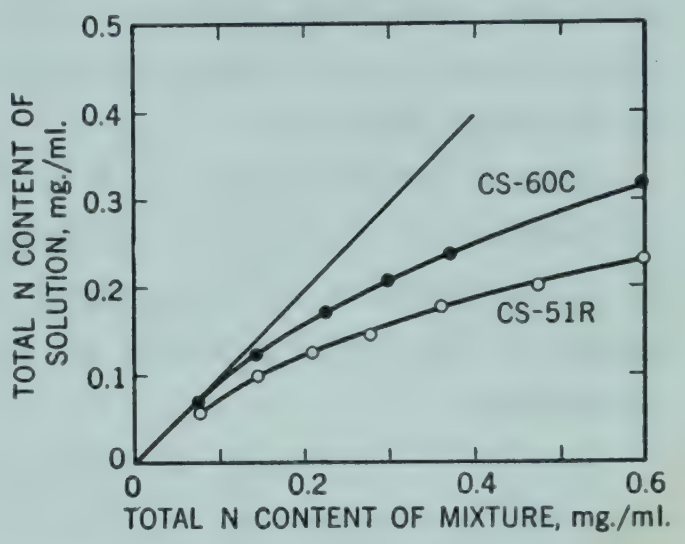


Fig. 99. Solubility of water-soluble allergenic fractions from cottonseed meal in 0.05 *M* acid potassium phthalate solution buffered at *p*H 5.0.[10]

to permit effective chemical separation; however, it might be possible to demonstrate multiplicity of the components by conducting solubility measurements under conditions other than those specified. Since CS-60C and other fractions are water-soluble, an analysis of their solutions in a Tiselius electrophoresis apparatus might possibly show the presence of several components.

One of the important phases of the work on the water-soluble allergens of the cottonseed was the determination of their presence or absence in refined edible cottonseed oil and hydrogenated oil. Bernton *et al.*[12] were unable to demonstrate a correlation between cutaneous and clinical sensitiveness to edible cottonseed oil or to hydrogenated cottonseed oil. Further, they proved that the specific and exceedingly potent water-soluble allergens of the cottonseed were not present in refined cottonseed oil. These results are of particular significance, since a mere trace of the water-soluble allergens in these products would be sufficient to produce severe symptoms in individuals sensitive to these substances. They suggest that patients who are clinically sensitive only to water-soluble cottonseed allergens can safely be spared the inconvenience of attempting to avoid foods containing cottonseed oil. Likewise other seed oils probably contain no water-soluble allergens.

2. Water-Insoluble Allergens

It was recognized that the cottonseed contained several different allergens, and besides the water-soluble CS-1A type another type designated as "2CS" has been demonstrated by Spies *et al.*[13] The 2CS-type allergen is associated with the water-insoluble fractions of the cottonseed, namely, the globulin fractions. The limited investigation of the active components of 2CS prevents definite assignment of activity to the globulin fractions; however, it is suggested that the 2CS activity may be characteristic of globulins containing high amounts of arginine (20 to 30% of the total nitrogen).

The active principle of 2CS differs from that of CS-1A in that 90% of the activity is destroyed by heating at 100° C.; 2CS is not dialysable, nor is it precipitable by basic lead acetate. More work will be necessary to establish the total number of different types of allergens present in the cottonseed.

Lest the foregoing discussion give the impression that cottonseed is unusual in possessing allergenic activity, it should be pointed out that most oil-bearing seeds, such as castor beans, kapok seeds, black mustard seeds, flaxseeds, soybeans, etc., also contain allergens.

III. Amino Acid Content of Cottonseed Meal and Isolated Cottonseed Protein Fractions

A. General Consideration of Amino Acids

There are twenty-three generally accepted amino acids which are constituents of proteins. Other amino acids have been reported, but sufficient proof of identity has not been established for some of these, and others do not occur generally in proteins. Of the twenty-three accepted amino acids, only twenty-one can be expected to occur in the seed meal proteins, such as those of cottonseed, the exceptions being iodogorgoic acid and thyroxine.

1. Names, Structural Formulas, Molecular Weights, and Chemical Composition of Amino Acids

The names and structural formulas of the twenty-three accepted amino acids derived from proteins are given in Table 124. There has been much confusion in the literature concerning the configurational designation of amino acids. A special committee has made a thorough study of these controversial issues and has offered specific rules[14] for the proper configurational designation of amino acids derived from proteins and other sources. According to these rules[14] the amino acids derived from proteins

[14] H. B. Vickery, *J. Biol. Chem.*, **169**, 239–245 (1947).

belong to the L system (see Table 124), which denotes the spatial arrangements of the groups about the alpha carbon atom. The distinction between the stereoisomers of the amino acids is made by a prefixed small capital D or L to denote the configurational family to which the alpha carbon belongs. The optically inactive mixture or racemic compound is designated by the prefix DL, for example, DL-methionine. The reader is referred to the

TABLE 124

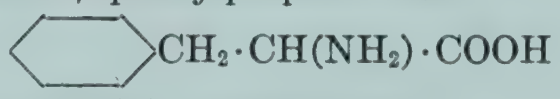
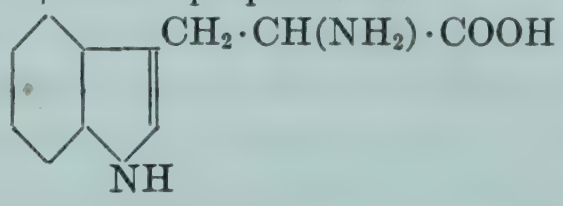
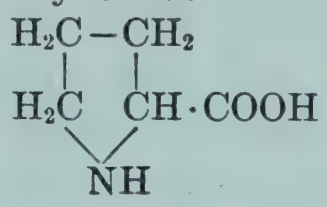
Names and Structural Formulas of the Generally Accepted Amino Acids Derived from Proteins

I. NEUTRAL AMINO ACIDS

Aliphatic

1. Glycine (inactive) or aminoacetic acid
$NH_2 \cdot CH_2 \cdot COOH$
2. L-Alanine or α-aminopropionic acid
$CH_3 \cdot CH(NH_2) \cdot COOH$
3. L-Norleucine or α-amino-*n*-caproic acid
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$
4. L-Valine or α-aminoisovaleric acid
$CH_3 \cdot CH(CH_3) \cdot CH(NH_2) \cdot COOH$
5. L-Leucine or α-aminoisocaproic acid
$CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot CH(NH_2) \cdot COOH$
6. L-Isoleucine or α-amino-β-methyl-*n*-valeric acid
$CH_3 \cdot CH_2 \cdot CH(CH_3) \cdot CH(NH_2) \cdot COOH$
7. L-Serine or α-amino-β-hydroxypropionic acid
$CH_2(OH) \cdot CH(NH_2) \cdot COOH$
8. L-Threonine or α-amino-β-hydroxybutyric acid
$CH_3 \cdot CH(OH) \cdot CH(NH_2) \cdot COOH$
9. L-Cystine or di-(α-amino-β-thiopropionic acid)
$HOOC \cdot CH(NH_2) \cdot CH_2 \cdot S \cdot S \cdot CH_2 \cdot CH(NH_2) \cdot COOH$
10. L-Cysteine or α-amino-β-thiolpropionic acid
$HS \cdot CH_2 \cdot CH(NH_2) \cdot COOH$
11. L-Methionine or α-amino-γ-methylthiol-*n*-butyric acid
$CH_3 \cdot S \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$

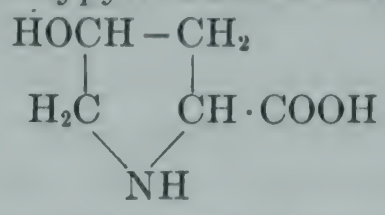
Cyclic

12. L-Phenylalanine or α-amino-β-phenylpropionic acid

13. L-Tryptophan or α-amino-β-indole propionic acid

14. L-Proline or pyrrolidine-α-carboxylic acid


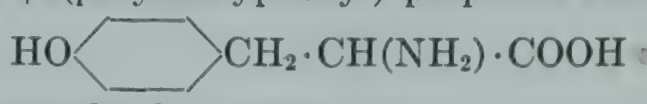
(*Table continued*)

TABLE 124 (*concluded*)

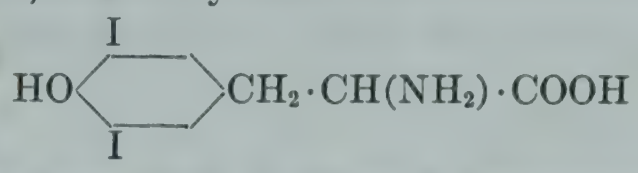
15. Hydroxy-L-proline or γ-hydroxypyrrolidine-α-carboxylic acid



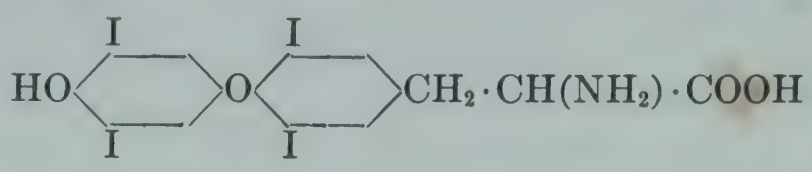
16. L-Tyrosine or α-amino-β-(p-hydroxyphenyl) propionic acid



17. L-Iodogorgoic acid or 3, 5-diiodotyrosine



18. L-Thyroxine or β-[3, 5-diiodo-4-(3′, 5′-diiodo-4′-hydroxyphenoxy) phenyl]-α-aminopropionic acid



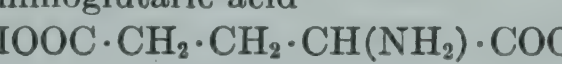
II. ACIDIC AMINO ACIDS

Aliphatic

19. L-Aspartic acid or aminosuccinic acid



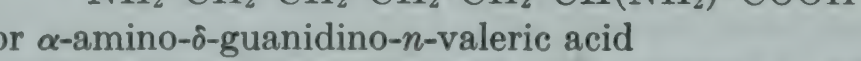
20. L-Glutamic acid or α-aminoglutaric acid



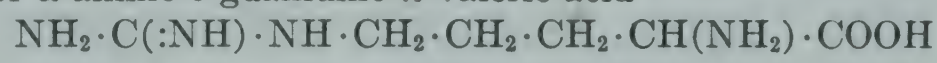
III. BASIC AMINO ACIDS

Aliphatic

21. L-Lysine or α-amino-ϵ-amino-n-caproic acid

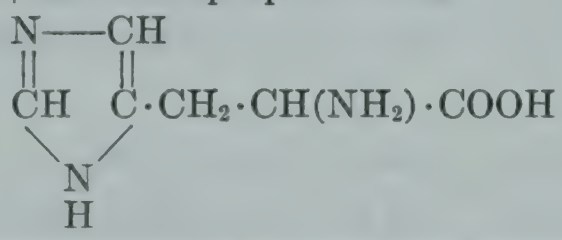


22. L-Arginine or α-amino-δ-guanidino-n-valeric acid



Cyclic

23. L-Histidine or α-amino-β-imidazolepropionic acid



original rules[14] for more detailed information. Since this chapter deals exclusively with amino acids derived from proteins it will be understood that these belong to the L system unless otherwise designated.

The chemical composition of the generally accepted amino acids derived from proteins is presented in Table 125.

From a nutritional standpoint, only eight of the twenty-three amino acids listed in Table 124, namely, L-threonine, L-valine, L-leucine, L-isoleucine, L-phenylalanine, L-lysine, L-tryptophan, and L-methionine, are re-

TABLE 125

Chemical Composition of the Generally Accepted Amino Acids

Amino acids	Molecular weight	Chemical composition, %				
		C	H	O	N	Other elements
Glycine	75.07	32.00	6.71	42.63	18.66	—
Alanine	89.09	40.44	7.92	35.92	15.72	—
Norleucine	131.17	54.94	9.99	24.39	10.68	—
Valine	117.15	51.26	9.46	27.32	11.96	—
Leucine	131.17	54.94	9.99	24.39	10.68	—
Isoleucine	131.17	54.94	9.99	24.39	10.68	—
Serine	105.09	34.28	6.71	45.68	13.33	—
Threonine	119.11	40.33	6.62	40.29	11.76	—
Cystine	240.29	29.99	5.03	26.63	11.66	S, 26.69
Cysteine	121.15	29.74	5.83	26.41	11.56	S, 26.46
Methionine	149.21	40.23	7.43	21.45	9.39	S, 21.49
Phenylalanine	165.19	65.44	6.71	19.37	8.48	—
Tryptophan	204.22	64.69	5.92	15.67	13.72	—
Proline	115.13	52.16	7.88	27.79	12.17	—
Hydroxyproline	131.13	45.79	6.92	36.61	10.68	—
Tyrosine	181.19	59.66	6.12	26.49	7.73	—
Iodogorgoic acid	433.01	24.96	2.10	11.09	3.23	I, 58.62
Thyroxine	776.93	23.19	1.42	8.24	1.80	I, 65.35
Aspartic acid	133.10	36.09	5.30	48.08	10.53	—
Glutamic acid	147.13	40.82	6.16	43.50	9.52	—
Lysine	146.19	49.30	9.65	21.89	19.16	—
Arginine	174.21	41.37	8.10	18.37	32.16	—
Histidine	155.16	46.44	5.85	20.62	27.09	—

quired to maintain nitrogen balance in man.[15] In addition to these eight amino acids, L-histidine is indispensable for the adult dog,[16] and L-histidine and L-arginine are needed for the rat.[17] Therefore, when discussing the amino acids nutritionally, they are referred to as "the ten essential amino acids."

Amino acids other than those listed in Table 125 have been found to be plant constituents and, therefore, may be expected to occur in proteins. In this group are Djenkolic acid, citrulline, canavanine, thiolhistidine, and dihydroxyphenylalanine, which have been isolated from Djenkol bean, watermelon tissue, beans, ergot, and bean seedlings, respectively. There is still another group of amino acids, such as aminobutyric acid, hydroxyvaline, hydroxylysine, norvaline, etc., which have not been suf-

[15] W. C. Rose, W. J. Haines, and J. E. Johnson, *J. Biol. Chem.*, **146,** 683–684 (1942). W. C. Rose, W. J. Haines, J. E. Johnson, and D. T. Warner, *ibid.*, **148,** 457–458 (1943), W. C. Rose, *Proc. Inst. Med.*, **15,** 24–25 (1944).

[16] W. C. Rose and E. E. Rice, *Science,* **90,** 186–187 (1939).

[17] M. Womack and W. C. Rose, *J. Biol. Chem.*, **116,** 381–391 (1936). M. Womack, W. S. Kemmerer, and W. C. Rose, *ibid.*, **121,** 403–410 (1937). W. C. Rose, *Physiol. Revs.*, **18,** 109–136 (1938). W. C. Rose and S. H. Eppstein, *J. Biol. Chem.*, **127,** 677–684 (1939).

ficiently investigated to permit their inclusion with the accepted natural amino acids. The discussion on the amino acid content of cottonseed meal and proteins will be limited to those amino acids which are in the accepted classification (Table 124).

2. Methods for the Determination of Amino Acids

The success of an amino acid determination depends to a great extent upon the method and conditions under which the protein is hydrolyzed. The most common methods of hydrolysis use either acid, alkali, or enzymatic digestion, or a combination of these. The method used will depend to a certain extent upon the particular amino acid being determined; for example, serine and threonine can be determined accurately only after acid hydrolysis of the protein, whereas alkali is suggested as the hydrolyzing agent if carbohydrates are present and if tyrosine and tryptophan are to be determined. Generally speaking, the extent of destruction of the various amino acids under hydrolyzing conditions has not been too thoroughly investigated; for further information, the reader is referred to the monograph of Block and Bolling [18] and other recent literature dealing with this subject.

The most accurate method for determining the quantity of an amino acid present in a given protein hydrolyzate is the isotope dilution method.[19-21] This method involves the addition of a pure amino acid containing isotopic nitrogen, N^{15}, in known proportion to a protein hydrolyzate, followed by the isolation from the hydrolyzate of a portion of the same amino acid in a pure state. The pure amino acid is analyzed for isotopic nitrogen, N^{15}. It is then possible by calculation to determine the amount of the particular amino acid present in the original hydrolyzate, since the proportion of isotopic nitrogen in the added amino acid will differ from that of the same amino acid isolated from the hydrolyzate according to the amount of this acid originally present. This method is not generally available because the use of a mass spectrograph is necessary for measurement of the isotopic nitrogen. The precision of this method, for the accurate determination of the amino acid content of a protein, depends upon the method used to hydrolyze the protein and upon the purity of the isolated amino acid.

The use of specific precipitants [22] in amino acid analysis of protein hydrolyzates has not proven to be as fruitful as had first appeared probable, according to a report of Stein and Moore.[23] Although these

[18] R. J. Block and D. Bolling, *The Amino Acid Composition of Proteins and Foods*, C. C Thomas, Springfield (Ill.), 1945.
[19] R. Schoenheimer and D. Rittenberg, *J. Biol. Chem.*, **127,** 285–290 (1939).
[20] D. Rittenberg and G. L. Foster, *J. Biol. Chem.*, **133,** 737–744 (1940).
[21] D. Shemin and G. L. Foster, *Ann. N. Y. Acad. Sci.*, **47,** 119–134 (1946).
[22] S. Moore, W. H. Stein, and M. Bergmann, *Chem. Revs.*, **30,** 423–432 (1942).
[23] W. H. Stein and S. Moore, *Ann. N. Y. Acad. Sci.*, **47,** 95–118 (1946).

precipitants, such as sulfonic acids, do not give a high degree of accuracy in the quantitative isolation of amino acids, they have been found to be of particular advantage in the isolation and purification of amino acids incident to the isotope dilution method.

Microbiological methods for amino acid analysis, based on the growth response of microörganisms, have recently received considerable impetus and appear to offer one of the best and most convenient methods of analysis. Brand [24] has recently shown that excellent agreement can be obtained between the microbiological assay and the isotope dilution methods. Stokes *et al.*[25] have shown that microbiological analysis for the ten essential amino acids can be made with 1.5 g. or less of protein. The fact that nine of these essential amino acids can be determined by using a single microörganism, *Streptococcus faecalis,* indicates the versatility of this method. Similar results may also be obtained with other microorganisms. An accumulation of results from this type of analysis will supply much needed information on the amino acid content of foods, animal feeds and isolated protein fractions.

Other methods—colorimetric, gravimetric, volumetric, spectrophotometric, chromatographic, etc.—have been used primarily by most investigators up to the present time. An evaluation of such methods has been published by Block and Bolling.[18] This latter group of methods has been used principally in the determination of the amino acid content of isolated cottonseed protein fractions, whereas the microbiological method has been used successfully for the analysis of cottonseed meal.

B. Amino Acid Content of Cottonseed Meal

The essentiality of proteins as food materials led to early attempts to determine the nutritive value of many feedstuffs. Since hydraulic- or expeller-pressed cottonseed meal has been a staple feed for many years, considerable attention has been given to the nutritive value of this commodity. It has been found,[26, 27] for instance, that the nutritive value of cottonseed meals varies considerably. It must, therefore, be emphasized that processing conditions are important factors in determining the nutritive value of cottonseed meals, since, upon analysis, no significant differences in amino acid content are consistently demonstrated. Thus, factors other than the mere presence of specific amino acids must be critically evaluated before assigning a nutritive index to a particular product. A knowledge of the amino acid content of a material containing proteins will, however, serve as a guide to its nutritive value.

[24] E. Brand, *Ann. N. Y. Acad. Sci.,* **47,** 187–228 (1946).
[25] J. L. Stokes, M. Gunness, I. M. Dwyer, and M. C. Caswell, *J. Biol. Chem.,* **160,** 35–49 (1945).
[26] H. S. Olcott and T. D. Fontaine, *Ind. Eng. Chem.,* **34,** 714–716 (1942).
[27] H. S. Olcott and T. D. Fontaine, *J. Nutrition,* **22,** 431–437 (1941).

The first amino acids of cottonseed meal to be determined quantitatively by a number of different investigators [28-32] were arginine, histidine, lysine, and cystine. While some of the results of earlier investigators, given in Table 126, do not differ appreciably from those obtained more recently, in general, they better serve to illustrate the wide differences in values that have been obtained by various analysts.

TABLE 126

Nitrogen Distribution[a] of the Total Proteins of Cottonseed Meals

Nitrogen	Grindley *et al.*[b]	Nollau[c]	Hamilton *et al.*[d,e]	Brewster and Alsberg[f]
Amide N	10.45	14.06	9.41	10.00
Humin N	7.78	6.27	6.30	10.97
Arginine N	19.52	12.77	18.71	19.73
Cystine N	0.65	2.74	0.94	1.11
Histidine N	5.47	7.57	7.17	3.87
Lysine N	4.78	1.94	4.21	6.69
Amino N of filtrate	42.82	45.02	40.72	43.50
Nonamino N of filtrate	5.43	7.49	2.87	5.23

[a] As per cent by weight of total meal nitrogen (Van Slyke method).
[b] H. S. Grindley, W. E. Joseph, and M. E. Slater, *J. Am. Chem. Soc.*, **37**, 1778–1781 (1915).
[c] E. H. Nollau, *J. Biol. Chem.*, **21**, 611–614 (1915).
[d] T. S. Hamilton, W. B. Nevens, and H. S. Grindley, *J. Biol. Chem.*, **48**, 249–272 (1921).
[e] W. B. Nevens, *J. Dairy Sci.*, **4**, 375–400 (1921).
[f] J. F. Brewster and C. L. Alsberg, *J. Biol. Chem.*, **37**, 367–371 (1919).

After these initial investigations, approximately twenty years elapsed before another concerted effort was made to determine contents of the different amino acids in cottonseed meal. The direction of wartime research upon this nation's protein resources and the improvement in methods of analysis are responsible for our present knowledge.

In Table 127 are given the results of the analysis of cottonseed meals for fourteen of the accepted amino acids. These results, which account for approximately 70% of the total meal nitrogen and include the ten nutritionally essential amino acids, are presented in such a manner that they will be of equal significance to the nutritionist and the fundamental investigator. The results have been reduced to a common basis—that is, to grams of amino acid per 100 grams of meal nitrogen—which eliminates differences in the nitrogen content of various meal samples and makes comparisons of different proteinaceous materials possible. Anyone desiring

[28] H. S. Grindley, W. E. Joseph, and M. E. Slater, *J. Am. Chem. Soc.*, **37**, 1778–1781 (1915).
[29] E. H. Nollau, *J. Biol. Chem.*, **21**, 611–614 (1915).
[30] T. S. Hamilton, W. B. Nevens, and H. S. Grindley, *J. Biol. Chem.*, **48**, 249–272 (1921).
[31] W. B. Nevens, *J. Dairy Sci.*, **4**, 375–400 (1921).
[32] J. F. Brewster and C. L. Alsberg, *J. Biol. Chem.*, **37**, 367–371 (1919).

to express these results as percentage of the total meal nitrogen due to a particular amino acid may do so with the aid of Table 125, in which the per cent of nitrogen in each amino acid is given, and by following the instructions given in the footnotes of Table 127.

Block and Bolling [18] have critically examined the analytical methods in general use for amino acid analysis, except the isotope dilution and microbiological methods. The results of the work of the same authors [33] on cottonseed meal (Table 127) may be considered to be of a high degree

TABLE 127

Amino Acid Content of Cottonseed Meal

Amino acid	Grams amino acid per 100 g. meal nitrogen,[a,b]	Amino acid	Grams amino acid per 100 g. meal nitrogen,[a,b]
Arginine	46.2,[c] 47.0[d]	Methionine	10.0,[c] 7.8[d]
Histidine	16.2,[c] 17.2[d]	Threonine	18.8,[c] 17.2[d]
Lysine	16.9,[c] 23.4[d]	Serine	28.1[d]
Tryptophan	8.1,[c] 9.0,[d] 6.3[e]	Leucine	31.2,[f] 34.4[d]
Tyrosine	20.0,[c] 9.4[d]	Isoleucine	21.2,[f] 28.1[d]
Phenylalanine	42.5,[c] 34.4[d]	Valine	23.2,[f] 28.1[d]
Glycine	33.1[c]	Glutamic acid	111.0,[g] 106.0[d]
Cystine	12.5[c]		

[a] Numerical values listed in this column multiplied by the percentage nitrogen content of a particular amino acid (see Table 125) will give the percentage of total meal nitrogen accounted for by that amino acid. For example, 46.2 g. arginine × 32.16% = 14.9% of the total meal nitrogen as arginine.

[b] Data reported under references (*c*) and (*e*) were obtained by chemical methods. Other data were obtained by microbiological assay techniques, which are considered to be more accurate in most cases than the chemical methods.

[c] R. J. Block and D. Bolling, *J. Am. Dietet. Assoc.*, **20**, 69–76 (1944).

[d] W. Baumgarten, A. N. Mather, and L. Stone, *Cereal Chem.*, **23**, 135–155 (1946).

[e] M. J. Horn and D. B. Jones, *J. Biol. Chem.*, **157**, 153–160 (1945).

[f] K. A. Kuiken, W. H. Norman, C. M. Lyman, F. Hale, and L. Blotter, *J. Biol. Chem.*, **151**, 615–625 (1943).

[g] C. M. Lyman, K. A. Kuiken, L. Blotter, and F. Hale, *J. Biol. Chem.*, **157**, 395–405 (1945).

of accuracy. Horn and Jones [34] determined the tryptophan and content of cottonseed flour (Proflo). Baumgarten *et al.*[35] obtained their results by microbiological assay methods using *Lactobacillus arabinosus, L. casei,* and *Streptococcus faecalis* as the assaying organisms—and Kuiken *et al.*[36] and Lyman *et al.*,[37] by using *L. arabinosus*. Some noticeable discrepancies in results of the various authors do exist. However, in general, the results obtained by microbiological assay methods are to be preferred.

The content of the nutritionally essential amino acids in the nitrogenous

[33] R. J. Block and D. Bolling, *J. Am. Dietet. Assoc.*, **20**, 69–76 (1944).

[34] M. J. Horn and D. B. Jones, *J. Biol. Chem.*, **157**, 153–160 (1945).

[35] W. Baumgarten, A. N. Mather, and L. Stone, *Cereal Chem.*, **23**, 135–155 (1946).

[36] K. A. Kuiken, W. H. Norman, C. M. Lyman, F. Hale, and L. Blotter, *J. Biol. Chem.*, **151**, 615–626 (1943).

[37] C. M. Lyman, K. A. Kuiken, L. Blotter, and F. Hale, *J. Biol. Chem.*, **157**, 395–405 (1945).

constituents of cottonseed meal, as reported by Baumgarten *et al.*[35] in Table 128, compares very favorably with that of other feeds, such as soybean meal, wheat, and corn, but is inferior to that of dehydrated grass or casein. Since casein is considered a nutritionally well-balanced protein source, cottonseed, by comparison, is deficient in or borders on a deficiency in lysine, methionine, threonine, and leucine. A comparison can be made with the other feeds on the basis that cottonseed meal contains an adequate amount of the remaining essential amino acids.

TABLE 128

Approximate Amino Acid Composition of Feeds,[a] Calculated to Grams of Amino Acid per 100 Grams of Feed Nitrogen[b]

Amino acid	Cotton-seed meal	Extracted soybean meal	Expelled soybean meal	Wheat	Corn	Casein	Dehy-drated grass
Arginine	47.0	33.0	36.8	19.2	26.7	25.8	42.0
Histidine	17.2	18.7	15.8	15.4	20.0	26.4	19.4
Lysine	23.4	33.0	42.2	15.4	20.0	54.8	45.2
Tryptophan	6.3	6.6	6.6	7.7	3.3	6.5	12.9
Tyrosine	9.4	13.2	11.8	3.8	1.3	34.8	19.4
Phenylalanine	34.4	30.8	29.0	26.9	33.3	32.9	54.8
Methionine	7.8	9.9	5.3	7.7	13.3	20.0	12.9
Threonine	17.2	23.1	29.0	15.4	20.0	29.0	42.0
Serine	28.1	26.4	29.0	26.9	53.4	43.8	38.7
Leucine	34.4	49.5	52.7	38.5	93.2	69.7	84.0
Isoleucine	28.1	38.5	38.2	26.9	40.0	51.5	58.0
Valine	28.1	33.0	34.2	26.9	33.3	50.3	64.5
Glutamic acid	106.0	99.0	103.0	150.0	140.0	145.0	122.5

[a] On a dry basis cottonseed meal contained: 6.4% nitrogen; extracted soybean meal, 9.1%; expelled soybean meal, 7.6%; wheat, 2.6%; corn, 1.5%; casein, 15.5%; dehydrated grass, 3.1%.

Numerical values listed in this table multiplied by the percentage nitrogen content of a particular amino acid (see Table 125) will give the percentage of total feed nitrogen accounted for by that amino acid. For example, in cottonseed meal, 47.0 g. arginine × 32.16% = 15.1% of the total feed nitrogen as arginine.

[b] W. Baumgarten, A. N. Mather, and L. Stone, *Cereal Chem.*, **23,** 135–155 (1946).

C. Amino Acid Content of Isolated Cottonseed Protein Fractions

Three of the protein fractions isolated by Jones and Csonka [4]: α-globulin, β-globulin, and pentose protein, were further characterized by a determination of their nitrogen distribution (Table 129). These results are, of course, inadequate for complete identification of the proteins, but they do indicate that the pentose protein differs appreciably from the other two fractions.

Analyses of two other protein fractions, prepared by Friedemann,[38] are also included in Table 129 because they were performed by the same method employed by Jones and Csonka. These two crude protein fractions, representing 62 and 55% of the total meal nitrogen, respectively, were

[38] W. G. Friedemann, *J. Biol. Chem.*, **51,** 17–20 (1922).

isolated from a 0.2% sodium hydroxide extract of cottonseed meal and from a 5% barium hydroxide extract by precipitation with acetic acid. Both protein fractions can be considered to consist primarily of α-globulin and β-globulin with a small amount of glutelin and pentose protein.

TABLE 129

Nitrogen Distribution[a] of Isolated Protein Fractions Prepared from Solvent-Extracted Cottonseed Meal

Nitrogen	α-Globulin[b]	β-Globulin[b]	Pentose protein[b]	0.2% NaOH-soluble, average acid precipitate[c]	5.0% $Ba(OH)_2$-soluble, average acid precipitate[c]
Amide N	11.40	11.70	12.99	10.54	10.47
Humin N	1.66	1.87	4.62	2.09	2.18
Cystine N	0.54	0.51	1.43	1.11	1.25
Arginine N	22.90	23.94	23.02	23.48	24.04
Histidine N	5.27	6.15	3.09	4.94	5.49
Lysine N	4.07	4.36	8.54	5.10	4.52
Amino N of filtrate	51.53	50.11	43.93	51.26	51.03
Nonamino N of filtrate	2.58	1.90	1.03	2.15	1.42
N in protein (ash and water free)	18.22	17.77	12.64	15.98	16.75

[a] As per cent by weight of total meal nitrogen (Van Slyke method).
[b] D. B. Jones and F. A. Csonka, *J. Biol. Chem.*, **64,** 673–683 (1925).
[c] W. G. Friedemann, *J. Biol. Chem.*, **51,** 17–20 (1922).

Unfortunately, from the fundamental viewpoint, the majority of amino acid analyses have been performed on cottonseed protein fractions which are much less clearly defined than those represented as α-globulin and β-globulin. From an industrial standpoint, however, the proteins which are of major interest are necessarily those which can be economically produced and would, in general, represent mixtures of several entities. In the case of cottonseed, such a protein preparation would undoubtedly consist primarily of the protein designated β-globulin, along with α-globulin, and varying amounts of the glutelin and pentose proteins.

In Table 130 are given the analyses in terms of amino acids obtained by several investigators [34, 39-49] on cottonseed protein preparations of vary-

[39] T. B. Osborne, C. S. Leavenworth, and C. A. Brautlecht, *Am. J. Physiol.*, **23,** 179–200 (1908).
[40] H. B. Vickery, *J. Biol. Chem.*, **132,** 325–341 (1940).
[41] O. Folin and A. D. Marenzi, *J. Biol. Chem.*, **83,** 89–102 (1929).
[42] D. B. Jones, C. E. F. Gersdorff, and O. Moeller, *J. Biol. Chem.*, **62,** 183–195 (1924).
[43] H. Zahnd and H. T. Clarke, *J. Biol. Chem.*, **102,** 171–182 (1933).
[44] E. Brand, F. J. Ryan, and E. M. Diskant, *J. Am. Chem. Soc.*, **67,** 1532–1534 (1945).
[45] E. Abderhalden and O. Rostoski, *Z. physiol. Chem.*, **44,** 265–275 (1905).
[46] T. B. Osborne and D. B. Jones, *Am. J. Physiol.*, **26,** 305–328 (1910).
[47] H. S. Olcott, *J. Biol. Chem.*, **153,** 71–82 (1944).
[48] T. D. Fontaine, H. S. Olcott, and A. Lowy, *Ind. Eng. Chem.*, **34,** 116–118 (1942).
[49] D. D. Van Slyke, A. Hiller, and D. A. MacFadyen, *J. Biol. Chem.*, **141,** 681–705 (1941).

ing degrees of purity. The results reported by Osborne *et al.*,[39] Vickery,[40] Folin and Marenzi,[41] Jones *et al.*,[42] Zahnd and Clarke,[43] and Brand *et al.*[44] were probably all obtained on a highly purified whole globulin fraction (α-globulin plus β-globulin). Such a fraction contained 18.6% nitrogen as prepared in Osborne's laboratory. The protein analyzed by Abderhalden and Rostoski [45] is assumed, for purposes of calculation, to have contained

TABLE 130

Amino Acid Content of Isolated Cottonseed Protein Fractions Prepared from Solvent-Extracted Cottonseed Meal[a]

Amino acid	Grams amino acid per 100 g. protein nitrogen [b]
Arginine	68.8, 68.8, 76.3[c]; 80.0[d]; 72.5[e]
Histidine	16.8, 18.9, 16.3[c]; 18.6[e]
Lysine	32.5, 31.9, 27.5[c]; 11.1[e]
Tryptophan	7.8, 8.0, 8.4[c]; 7.3[g]; 13.9[h]; 7.2[i]
Tyrosine	21.0, 20.8, 17.9[c]; 19.4[g]; 12.3[j]
Phenylalanine	48.5, 46.8, 51.0[c]; 21.0[j]
Glycine	6.4[j]
Alanine	24.1[j]
Cystine	6.6, 6.5, 6.7[c]; 6.1[h]; 7.2[k]; 4.7[l]
Methionine	15.0, 18.7, 9.5[c]
Serine	17.4, 17.1, 16.2[c]; 2.1[j]
Threonine	17.4, 17.1, 16.2[c]
Leucine[m]	51.0, 53.2, 46.8[c]; 34.4[n]
Isoleucine[m]	13.2, 14.2, 14.0[c]
Valine	36.6, 36.1, 41.8[c]
Glutamic acid	92.5[j], 132.5[l]
Aspartic acid	15.6[j]
Proline	12.4[j]

[a] The result reported by Brand *et al.*, footnote (*n*), was obtained by microbiological assay. All other results reported in this table were obtained by chemical methods.

[b] Numerical values listed in this column multiplied by the percentage nitrogen content of a particular amino acid (see Table 125) will give the percentage of total protein nitrogen accounted for by that amino acid. For example, 68.8 g. arginine × 32.16% = 22.1% of the total protein nitrogen as arginine.

[c] T. D. Fontaine, H. S. Olcott, and A. Lowy, *Ind. Eng. Chem.*, **34**, 116–118 (1942). The three references indicate results on three different protein preparations. See text.

[d] H. B. Vickery, *J. Biol. Chem.*, **132**, 325–341 (1940).

[e] T. B. Osborne, C. S. Leavenworth, and C. A. Brautlecht, *Am. J. Physiol.*, **23**, 179–200 (1908).

[f] Van Slyke *et al.*, footnote (*o*), reported cottonseed globulin to contain 0.23% hydroxylysine.

[g] O. Folin and A. D. Marenzi, *J. Biol. Chem.*, **83**, 89–102 (1929).

[h] D. B. Jones, C. E. F. Gersdorff, and O. Moeller, *J. Biol. Chem.*, **62**, 183–195 (1924).

[i] M. J. Horn and D. B. Jones, *J. Biol. Chem.*, **157**, 153–160 (1945).

[j] E. Abderhalden and O. Rostoski, *Z. physiol. Chem.*, **44**, 265–275 (1905). Results are considered to be in error due to the method used in the determination. Abderhalden's results are considered to be minimum values.

[k] H. Zahnd and H. T. Clarke, *J. Biol. Chem.*, **102**, 171–182 (1933).

[l] H. S. Olcott, *J. Biol. Chem.*, **153**, 71–82 (1944).

[m] Leucine values reported by Fontaine *et al.* are probably high and isoleucine values low because of the lack of dependability of the chemical method used. A lower value was obtained by Brand *et al.* for leucine by microbiological assay.

[n] E. Brand, F. J. Ryan, and E. M. Diskant, *J. Am. Chem. Soc.*, **67**, 1532–1534 (1945).

[o] D. D. Van Slyke, A. Hiller, and D. A. MacFadyen, *J. Biol. Chem.*, **141**, 681–705 (1941).

18.6% nitrogen, since the percentage of nitrogen was not indicated in their work. As a result of the amino acid ester distillation method used by Abderhalden and Rostoski, their results are necessarily minimum values, as shown by the later work of Osborne and Jones.[46] Horn and Jones [34] analyzed a purified globulin fraction containing 18.0% nitrogen. A very crude protein fraction, containing only 14.8% nitrogen, analyzed by Olcott [47] represents the total protein extractable from solvent-extracted cottonseed meal with a sodium hydroxide solution at *p*H 11.0, and precipitable at *p*H 4.0 from the clarified extract.

A rather extensive analysis of three isolated cottonseed protein fractions has been reported by Fontaine *et al.*[48] (Table 130). Thirteen different amino acids were determined by methods which appeared to be the best substantiated at the time the analyses were being conducted. Each protein fraction was prepared from water-washed solvent-extracted meal. The water-washing of the meal resulted in the removal of approximately 20% of the total meal nitrogen which would account for almost all of the nonprotein nitrogen and the pentose protein fraction. Preparations designated "I" and "II" by the authors were obtained by extracting the water-washed meal with a sodium hydroxide solution at *p*H 10.5, and by precipitating the protein from the clarified extract at *p*H 6.0. Preparation II was redissolved at *p*H 10.5 and reprecipitated at *p*H 6.0. The yield of each

TABLE 131

Amino Acid Content of Allergenic Fractions from Cottonseed[a]

Form of nitrogen	Fraction[b]		
	CS-51R	CS-52R	CS-56H
Humin	0.1	0.1	1.1
Ammonia	15.0	14.9	9.9
Cystine[c]	4.5	4.9	4.3
Histidine	0.1	0.1	—
Arginine	32.8	33.2	29.5
Lysine	3.8	1.6	2.0
Glutamic acid	14.2	14.2	11.4
Tyrosine	1.7	1.8	1.3
Tryptophan[d]	1.4	—	—
Monoamino fraction	8.0	—	11.2
Dicarboxylic acid fraction	3.5	—	7.4
Total	85.1	70.8	78.1

[a] J. R. Spies, *J. Am. Chem. Soc.*, **63**, 2994–2996 (1941). Results are expressed in terms of per cent of total nitrogen.

[b] Fractions CS-51R, CS-52R and CS-56H contained 19.8, 20.2, and 11.6% nitrogen; 2.29, 2.24, and 2.04% sulfur; and 0.9, 0.9, and 36.6% carbohydrate, respectively. All analyses are on ash- and water-free basis.

[c] Cystine in CS-51R and CS-52R accounted for all of the sulfur content, but cystine in CS-56H accounted for only 55% of the total sulfur.

[d] J. R. Spies and E. J. Coulson, *J. Am. Chem. Soc.*, **65**, 1720–1729 (1943), reported that tryptophan accounts for 1.1 to 1.4% of the total nitrogen of Fraction CS-51R.

protein preparation, consisting of globulins and glutelin, accounted for only approximately 35% of the total original meal nitrogen. The preparation designated as "III" was obtained by extracting the water-washed meal with 3% sodium chloride solution, and precipitating the globulin fraction by dilution of the clarified extract with four volumes of water. The precipitated protein was washed and, when dried, accounted for only approximately 25% of the total original meal nitrogen. The results of the amino acid analyses of Preparations I, II, and III, containing 16.7, 16.9,

TABLE 132

Approximate Amino Acid Composition of Proteins Calculated to Grams of Amino Acid per 100 Grams of Protein Nitrogen[a]

Amino acid	Cotton-seed globulin	Arachin (peanut)	Cona-rachin (peanut)	Edestin (hemp)	Glycinin (soybean)	Ricin (castor bean)	Casein[b]
Arginine	80.0[c]	76.3[c]	80.0[d]	86.3[e]	53.1[f]	73.2[g]	25.8
Histidine	18.9[h]	10.3[d]	10.0[d]	11.2[e]	20.6[f]	0.0[g]	26.4
Lysine	31.9[h]	27.3[d]	33.0[d]	11.9[e]	—	39.4[g]	54.8
Tryptophan	8.0[h]	3.8[i]	5.1[i]	8.7[j]	10.0[f]	2.5[g]	6.5
Tyrosine	20.8[h]	31.5[i]	15.9[i]	20.0[j]	11.2[f]	16.9[g]	34.8
Phenylalanine	46.8[h]	28.0[i]	18.3[i]	21.3[k]	—	—	32.9
Cystine	6.5[h]	8.4[i]	16.2[i]	6.9[l]	9.4[m]	—	—
Methionine	18.7[h]	3.7[i]	11.8[i]	12.5[l]	10.6[m]	—	20.0
Threonine	17.1[h]	14.2[i]	11.2[i]	—	—	16.9[g]	29.0
Serine	17.1[h]	28.8[i]	27.7[i]	—	—	—	43.8
Leucine	34.4[n]	—	—	41.2[o]	—	93.8[g]	69.7
Isoleucine	14.2[h]	—	—	—	—		51.5
Valine	36.1[h]	—	—	31.9[o]	—	12.5[p]	50.3
Glutamic acid	132.5[q]	106.2[r]	—	111.0[s]	108.8[r]	118.8[g]	145.0

[a] Much of the data reported in this table on seed meal proteins will possibly be revised when further analyses are made by the microbiological assay methods. Numerical values listed in this table multiplied by the percentage nitrogen content of a particular amino acid (see Table 125) will give the percentage of total protein nitrogen accounted for by that amino acid. For example, cottonseed, 80.0 g. arginine × 32.16% = 25.7% of the total protein nitrogen as arginine.

[b] W. Baumgarten, A. N. Mather, and L. Stone, *Cereal Chem.*, **23**, 135–155 (1946).

[c] H. B. Vickery, *J. Biol. Chem.*, **132**, 325–341 (1940).

[d] C. O. Johns and D. B. Jones, *J. Biol. Chem.*, **30**, 33–38 (1917).

[e] H. B. Vickery and C. S. Leavenworth, *J. Biol. Chem.*, **76**, 707–722 (1928).

[f] A. Kiesel and M. Znamenskaja, *Z. physiol. Chem.*, **213**, 89–108 (1932).

[g] P. Karrer, A. P. Smirnoff, H. Ehrensperger, J. van Slooten, and M. Keller, *Z. physiol. Chem.*, **135**, 129–166 (1924).

[h] T. D. Fontaine, H. S. Olcott, and A. Lowy, *Ind. Eng. Chem.*, **34**, 116–118 (1942).

[i] W. L. Brown, *J. Biol. Chem.*, **142**, 299–301 (1942); **154**, 57–61 (1944); **155**, 277–282 (1944).

[j] A. Kiesel and S. Kuzmin, *Z. physiol. Chem.*, **238**, 145–148 (1936).

[k] R. Kapeller-Adler, *Biochem. Z.*, **252**, 185–200 (1932).

[l] K. Bailey, *Biochem. J.*, **31**, 1396–1405 (1937).

[m] H. D. Baernstein, *J. Biol. Chem.*, **97**, 663–668 (1932).

[n] E. Brand, F. J. Ryan, and E. M. Diskant, *J. Am. Chem. Soc.*, **67**, 1532–1534 (1945).

[o] C. Fromegeot and M. Mourgue, *Enzymologia*, **9**, 329–336 (1941).

[p] A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, **35**, 294–312 (1941).

[q] H. S. Olcott, *J. Biol. Chem.*, **153**, 71–82 (1944).

[r] D. B. Jones and O. Moeller, *J. Biol. Chem.*, **79**, 429–441 (1928).

[s] A. C. Chibnall, M. W. Rees, and E. F. Williams, *Biochem. J.*, **37**, 372–388 (1941).

and 17.9% nitrogen, respectively, are given in chronological order in Table 130. There is fair agreement in the results of amino acid analyses obtained by various investigators on cottonseed globulin fractions of varying degrees of purity. Attempts have been made to indicate those results which are known to be in considerable error, while other results, because of insufficient information, cannot be critically evaluated.

Three cottonseed allergenic fractions, for which Spies [50] and Spies and Coulson [11] report a limited number of amino acid analyses, are of considerable interest. The analytical results, given in Table 131, show that the allergenic fractions contain more arginine and cystine, and less histidine and lysine than do any other protein fraction isolated from cottonseed. In an earlier part of this chapter, it was pointed out that the cystine and sulfur contents of these fractions are very high for plant proteins. In addition, no methionine was detected in these fractions.

In Table 132, the approximate amino acid composition of an "average" cottonseed globulin is compared with the composition of similar globulin preparations obtained from hempseed, peanuts, soybeans, castor beans, and casein.[51–63] Nutritionally, cottonseed globulin appears to be deficient in or borders on deficiency in lysine, threonine, leucine, and possibly isoleucine, although, in the latter case, it is believed that the isoleucine value reported is too low.

IV. Solubility Characteristics of Cottonseed Proteins

Approximately 2 million tons of cottonseed meal are produced annually in the United States by expression in hydraulic or expeller presses. Only recently have serious attempts been started [64] to produce oil-free cottonseed meal by commercial solvent extraction. This new development of solvent extraction is of particular advantage if the meal proteins are to be used for purposes other than as a cattle feed. The reason is that the application of high temperatures in the presence of high moisture causes

[50] J. R. Spies, *J. Am. Chem. Soc.*, **63,** 2994–2996 (1941).
[51] C. O. Johns and D. B. Jones, *J. Biol. Chem.*, **30,** 33–38 (1917).
[52] W. L. Brown, *J. Biol. Chem.*, **142,** 299–301 (1942); **154,** 57–61 (1944); **155,** 277–282 (1944).
[53] D. B. Jones and O. Moeller, *J. Biol. Chem.*, **79,** 429–441 (1928).
[54] H. B. Vickery and C. S. Leavenworth, *J. Biol. Chem.*, **76,** 707–722 (1928).
[55] A. Kiesel and S. Kunzmin, *Z. physiol. Chem.*, **238,** 145–148 (1936).
[56] R. Kapeller-Adler, *Biochem. Z.*, **252,** 185–200 (1932).
[57] K. Bailey, *Biochem. J.*, **31,** 1396–1405 (1937).
[58] C. Fromageot and M. Mourgue, *Enzymologia*, **9,** 329–336 (1941).
[59] A. C. Chibnall, M. W. Rees, and E. F. Williams, *Biochem. J.*, **37,** 372–388 (1941).
[60] H. D. Baernstein, *J. Biol. Chem.*, **97,** 663–668 (1932).
[61] A. Kiesel and M. Znamenskaja, *Z. physiol. Chem.*, **213,** 89–108 (1932).
[62] P. Karrer, A. P. Smirnoff, H. Ehrensperger, J. van Slooten, and M. Keller, *Z. physiol. Chem.*, **135,** 129–166 (1924).
[63] A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, **35,** 294–312 (1941).
[64] *Oil & Soap*, **22,** 11 (1945).

a considerable denaturation (decrease in solubility) of the meal proteins. Thus the heat treatment used in the hydraulic- and expeller-pressing methods renders the proteins virtually worthless from the standpoint of protein isolation and industrial utilization. To fully understand the extent of the denaturation of the proteins by these methods, it is first necessary to know the solubility characteristics of the undenatured proteins of cottonseed and the factors which may influence the solubility of the proteins.

The solubility characteristics of the nitrogenous constituents of solvent-extracted cottonseed meals and commercial expressed meals in aqueous salt, acid, and alkali solutions, and combinations of these solutions, have been determined by Olcott and Fontaine.[26, 65-67] The effects of various acids at relatively high concentrations and of dialyzable meal constituents on the solubility of the nitrogenous constituents of solvent-extracted cottonseed meal have been investigated by Fontaine and co-workers.[68] Phytic acid (inositol hexaphosphoric acid), a naturally occurring substance in cottonseed meal and other seed meals, has been shown by Fontaine *et al.*[5] to affect the solubility of the nitrogenous constituents of cottonseed meal at acid *p*H values.

A. Solvent-Extracted Cottonseed Meal

1. Composition of Cottonseed Meal and Solubility Methods

A typical analysis[65] of cottonseed meal prepared by batch solvent extraction of cottonseed flakes with ethyl ether is as follows:

Constituent	Per cent
Water	9.0
Nitrogen	8.6
Lipids	0.5 (ethyl ether extraction)
Lipids	2.0 (chloroform extraction)
Ash	7.5

On a moisture-, lipid-, and ash-free basis, cottonseed meal contains approximately 10.6% nitrogen.

In the discussion which follows, the nitrogenous constituents of the meal are divided into several categories:

(*a*) Nonprotein nitrogen, comprising approximately 10% of the total meal nitrogen, soluble in all solutions and at all *p*H values.

[65] H. S. Olcott and T. D. Fontaine, *J. Am. Chem. Soc.*, **61,** 2037–2040 (1939).
[66] H. S. Olcott and T. D. Fontaine, *J. Am. Chem. Soc.*, **62,** 1334–1339 (1940).
[67] H. S. Olcott and T. D. Fontaine, *J. Am. Chem. Soc.*, **62,** 3519 (1940).
[68] T. D. Fontaine, G. W. Irving, Jr., and K. S. Markley, *Ind. Eng. Chem.*, **38,** 658–662 (1946).

(*b*) Carbohydrate-rich protein nitrogen, comprising approximately 10% of the total meal nitrogen. Soluble in water and in salt solutions at all *p*H values more alkaline than a *p*H of 6.0, but insoluble at *p*H 3.5 in the absence of added salts.

(*c*) Globulin protein nitrogen, comprising approximately 60% of the total meal nitrogen. Maximum solubility usually in 0.5 to 1.0 *N* salt solutions. Completely soluble in sodium hydroxide solutions at *p*H 9.0 and above, but completely insoluble between *p*H 2.0 and 7.0 in the absence of added salts.

(*d*) Glutelin protein nitrogen, comprising approximately 15% of the total meal nitrogen. Soluble only at high *p*H values above 9.0, and insoluble at all other *p*H values and in salt solutions.

(*e*) Insoluble protein nitrogen, comprising approximately 5% of the total meal nitrogen. Insoluble under all conditions of extraction. It is conceivable that this fraction may represent denatured protein.

It should be understood that these are the groupings of the different nitrogen fractions in the presence of *all of the nonnitrogen meal constituents.* As has been stated previously, phytic acid influences the solubility of some of the nitrogenous constituents at acid *p*H values.

All the solubilities referred to above and in the following paragraphs

TABLE 133

Effect of Agitation and Temperature on Extraction of Nitrogenous Constituents from Solvent-Extracted Cottonseed Meal with 0.5 *N* Sodium Chloride[a]

Effect of Agitation

Time, min.	Total nitrogen extracted, %	
	By continuous agitation	With no agitation
30	75.5	73.6
60	75.5	74.4
90	76.6	76.2
120	77.0	77.3
180	—	78.2
1440	—	78.3

Effect of Temperature

Temperature, °C.	Total nitrogen extracted, %	
	By H_2O	By 0.5 *N* NaCl
0	26.0	55.2
25	28.3	79.7
50	29.8	81.9

[a] H. S. Olcott and T. D. Fontaine, *J. Am. Chem. Soc.*, **61**, 2037–2040 (1939).

were based upon the equilibration of 1 part of meal with 40 parts of aqueous solvent. After an allotted time, with occasional shaking, the meal suspension was centrifuged and the clear supernatant solution was analyzed for its nitrogen content. The solubility of the nitrogenous constituents was calculated on the basis of the total volume of solvent added rather than the volume recovered. This method is satisfactory for comparative purposes, but it should be pointed out that the meal retains roughly four times its weight of solvent after centrifugation.

The time necessary for equilibrium conditions to be established and the effect of temperature on the extraction of the nitrogenous constituents of cottonseed meal with 0.5 *N* sodium chloride solution are given in Table 133. Equilibrium is established within three hours, and the difference between extraction at 25° and 50° C. is insufficient to justify use of the higher temperature. In fact, when dealing with acid and alkaline extractions, the lower temperature is to be preferred. The 0.5 *N* sodium chloride extract includes the nonprotein and carbohydrate-protein fractions of the meal in addition to practically all of the globulin protein

TABLE 134

Effect of Salts on Peptization of Cottonseed Meal Proteins[a]

Salt	Percentage of total nitrogen extracted by solutions of normality and *p*H indicated			
	0.25 *N*	0.5 *N*	1.0 *N*	*p*H[b]
LiCl	53.4	81.2	81.8	6.4
NaF	—	57.5	73.2	7.2
NaCl	51.1	78.2	80.3	6.4
NaBr	59.1	81.5	—	6.4
NaI	68.0	81.9	—	6.4
Na_2SO_4	78.5	81.9	—	6.8
Na_2SO_3	82.8	82.8	82.1	8.3
$NaHCO_3$	—	77.7	—	8.0
Na_2HPO_4	57.9	79.4	—	8.2
NaH_2PO_4	—	28.1	35.6	5.3
Na acetate	—	65.9	78.4	7.0
Na citrate	—	77.0	—	7.4
Na oxalate	67.8	81.7	—	7.1
Na tartrate	55.9	79.2	77.6	6.9
KF	—	54.0	74.7	7.1
KCl	—	78.1	—	6.5
KBr	—	80.5	—	6.5
KI	—	81.9	81.9	6.5
$CaCl_2$	59.1	81.5	81.5	5.1
$MgCl_2$	60.9	82.3	82.9	5.5
$MgBr_2$	62.0	83.5	83.8	5.5
$MgSO_4$	58.9	82.0	82.3	5.7
$BaCl_2$	62.8	77.1	78.9	5.3

[a] H. S. Olcott and T. D. Fontaine, *J. Am. Chem. Soc.*, **61**, 2037–2040 (1939).

[b] *p*H for 0.5 *N* solutions; in general, the values for the other concentrations did not vary by more than 0.1 *p*H.

fraction; thus, approximately 20% of the total meal nitrogen in each salt extract represents nonglobulin protein nitrogen.

2. Extraction of the Nitrogenous Constituents of Cottonseed Meal with Various Salt Solutions

The peptizing activity of a number of different salts is shown in Table 134. In most cases the 0.5 *N* salt solution is as effective in extracting the nitrogenous constituents of the meal as is a 1.0 *N* solution of the same salt. Only at a low salt concentration (0.25 *N*) is there any marked lyotropic effect; that is, increased nitrogen solubility over the preceding salt of a homologous series, such as sodium fluoride, chloride, bromide, and iodide.

Sodium sulfite appeared to offer advantages as an extractant because the amount of nitrogen extracted was constant and much higher than that extracted by sodium hydroxide solution at *p*H 8.3. Upon decreasing the sodium sulfite concentration below 0.25 *N*, it was found (Table 135) that

TABLE 135

Effect of Salt Concentration on the Extraction of Proteins from Cottonseed Meal by Sodium Chloride and Sodium Sulfite Solutions[a]

Concentration of salt, normality of solution	Percentage of total nitrogen extracted		
	From ether-extracted meal with NaCl	From ether-extracted commercial meal with NaCl	From ether-extracted meal with Na_2SO_3
0.0	24.9	7.6	—
0.1	28.1	8.4	—
0.15	—	—	61.7
0.175	—	—	68.5
0.2	44.4	—	74.5
0.25	—	—	82.8
0.3	57.7	21.9	—
0.4	71.9	—	—
0.5	78.2	37.1	82.8
0.75	81.5	—	—
1.0	80.3	41.6	82.1
2.0	79.3	—	—
3.0	78.9	41.2	—
4.0	76.6	—	—
5.0	73.2	38.1	—

[a] H. S. Olcott and T. D. Fontaine, *J. Am. Chem. Soc.*, **61**, 2037–2040 (1939).

the extraction was less effective than at higher concentrations but that it was still much more effective than with sodium chloride solutions. Also included in this table are the data obtained on the solubility of the nitrogenous constituents of commercial hydraulic-pressed meal in sodium chloride solutions. The denaturation of the cottonseed proteins is illustrated by their decreased solubility; only about one-half as much nitrogen

is peptized by sodium chloride solutions from the hydraulic-pressed meal as from the solvent-extracted meal.

The foregoing results show that it is possible to extract about 80% of the total meal nitrogen with a number of different salt solutions. Approximately 75% of the extracted nitrogen can be recovered as a globulin fraction if the protein is precipitated at a suitable acid *p*H value.

3. Extraction of Nitrogenous Constituents of Cottonseed Meal with Acid and Alkali Solutions

The solubility of the nitrogenous constituents of a solvent-extracted cottonseed meal and of a commercial hydraulic-pressed meal at various acid and alkaline *p*H values is given in Table 136. Data are also included

TABLE 136

Effect of *p*H on the Extraction of Proteins from Cottonseed Meal[a]

Milliequivalents of acid or base per g. meal	Total nitrogen extracted					
	From ether-extracted meal		From ether-extracted meal with 0.5 *N* NaCl		From ether-extracted commercial meal	
	*p*H[b]	%	*p*H[b]	%	*p*H[b]	%
H_2SO_4						
3.60	1.9	23.6	1.5	22.9	1.9	7.2
1.80	2.3	18.1	2.0	24.9	2.3	6.4
1.17	2.9	12.9	2.9	27.1	2.8	5.4
0.81	3.8	13.6	3.8	28.9	3.7	4.8
0.45	4.8	18.1	4.7	38.8	4.8	5.6
0.18	5.8	22.8	5.6	72.1	5.9	6.8
0.0	6.9	24.9	6.4	78.2	6.8	7.6
NaOH						
0.10	7.6	32.9	6.9	78.4	7.4	14.6
0.21	8.7	73.8	7.5	78.7	8.6	38.1
0.31	9.6	85.6	8.8	78.4	—	—
0.41	10.4	90.0	9.1	78.7	10.0	55.1
0.62	10.7	91.4	9.9	79.5	10.3	60.4
0.82	11.1	93.1	10.5	78.4	—	—
1.03	11.4	92.8	10.8	78.0	11.1	64.4
3.09	11.9	92.6	11.5	82.9	11.7	68.4
4.12	12.0	90.9	—	—	—	—

[a] H. S. Olcott and T. D. Fontaine, *J. Am. Chem. Soc.*, **61**, 2037–2040 (1939).
[b] Adjusted by addition of sulfuric acid or sodium hydroxide to the solution.

to show the effect of *p*H and a constant amount of sodium chloride (0.5 *N*) on the peptization values of solvent-extracted cottonseed meal.

The solvent-extracted cottonseed meal *p*H–peptization curve, in the absence of added salts, is characterized by a very broad minimum solubility range (Fig. 100). Indeed, from knowledge of the protein components of cottonseed, it appears justifiable to state that there are in effect two minima for cottonseed proteins. The first minimum solubility range is *p*H

6.0 to 7.0 where the globulin and glutelin protein fractions are insoluble, and the second minimum is in the *p*H range 2.5 to 4.0 where the globulin, glutelin, and carbohydrate-rich protein fractions are insoluble; the difference in the nitrogen solubility at *p*H 3.5 and at *p*H 6.5 can be attributed to the carbohydrate-rich protein fraction. The *p*H–peptization curves for solvent-extracted soybean meal,[69] shown also in Figure 100, and for solvent-extracted peanut meal as observed by Fontaine and Burnett,[70] differ markedly from that of cottonseed meal. Soybean and peanut meals exhibit a narrow minimum solubility range, a high nitrogen solubility at low alkaline *p*H values, and a greater solubility in acid solution.

The solubility of the nitrogenous constituents of the hydraulic-pressed cottonseed meal (Fig. 100) is practically constant between *p*H 2.0 and 7.0

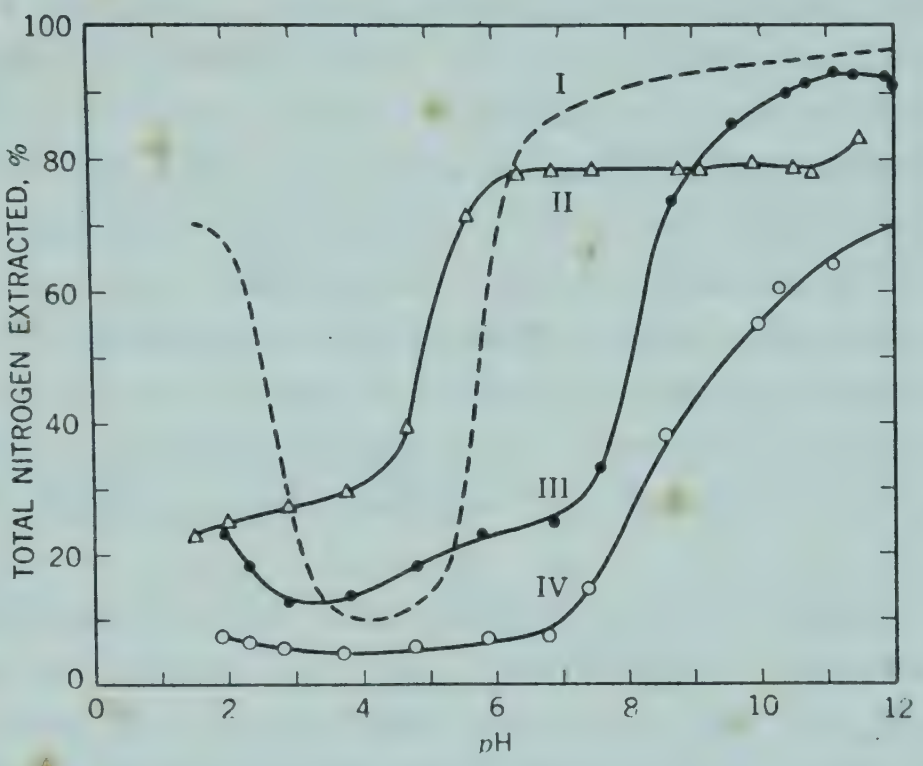


Fig. 100. Solubility of the nitrogenous constituents of oilseed meals at varying *p*H values: (I) soybean meal,[69] (II) ether-extracted cottonseed meal in 0.5 *N* sodium chloride,[65] (III) ether-extracted cottonseed meal,[65] and (IV) commercial hydraulic-pressed cottonseed meal, ether-extracted.[65]

and is vastly inferior to that of the solvent-extracted meal at higher alkaline *p*H values. This illustrates clearly the effect of processing conditions on the solubility of the proteins.

There is a certain similarity in the shapes of the *p*H–peptization curves for solvent-extracted cottonseed meal in the presence and in the absence of 0.5 *N* sodium chloride. It appears that the 0.5 *N* sodium chloride curve is merely displaced about four *p*H units toward the acid side; thus, if the nitrogenous constituents are extracted with 0.5 *N* sodium chloride solution at *p*H 6.9, the clarified extract must be adjusted to *p*H 3.0 in

[69] A. K. Smith and S. J. Circle, *Ind. Eng. Chem.*, **30,** 1414–1418 (1938).
[70] T. D. Fontaine and R. S. Burnett, *Ind. Eng. Chem.*, **36,** 164–167 (1944).

order to obtain the globulin protein fraction—as compared to a *p*H of 7.0, if an alkaline extract is obtained. Sodium chloride extraction has the natural advantage of extracting the protein practically at neutrality, but the disadvantage of having to subject the protein to precipitation at a very low acid *p*H value. Proteins isolated by this method are extremely insoluble. It is of particular interest to note that the extraction curve of cottonseed meal with 0.5 *N* sodium chloride solution is practically linear from *p*H 6.0 to 11.0, indicating a complete suppression of the solubility of the glutelin protein fraction.

Extraction of solvent-extracted cottonseed meal with sodium hydroxide solution at *p*H 10 to 11, in the absence of added salts, and precipitation of the protein at *p*H 6.0 has proved relatively satisfactory for the recovery of the combined globulin and glutelin protein fractions. However, considerable difficulty is encountered in centrifugation for recovery of the precipitate, since the precipitated protein has a tendency to be very slimy. This method suffers the further disadvantage that the cottonseed meal contains pigments which are easily oxidized at the very high *p*H employed for extraction. The oxidized pigments both react with and are adsorbed on the protein when the latter is precipitated at *p*H 6.0. The pigments are not easily removed, hence the protein is inclined to be highly colored. An exact evaluation of the color of the various proteins, as compared with peanut and soybean proteins, will be discussed in a later portion of this chapter.

Effect of Various Acids and Dialyzable Meal Constituents. In the initial investigations [65] detailed just above the solubility of the cottonseed meal proteins at acid *p*H values was determined with sulfuric acid only. These results differed considerably from those which had been obtained for peanut and soybean meal with hydrochloric acid as the peptizing agent. Accordingly, further investigations [68] of protein solubility were conducted on solvent-extracted cottonseed meal, dialyzed cottonseed meal, and isolated cottonseed protein using a variety of acids. Details of the preparation of the dialyzed meal and protein are given in a later section of this chapter.

The solubility of the nitrogenous constituents of solvent-extracted cottonseed meal in solutions of a number of strong acids, such as hydrochloric, sulfuric, and trichloroacetic acids, and in solutions of weaker acids, such as acetic and phosphoric acids, is shown in Figure 101. Hydrochloric acid peptizes a greater percentage of the protein of undialyzed meal than does sulfuric acid, but the difference is relatively small and does not suggest that any improvement in extraction would result from the use of hydrochloric acid. Trichloroacetic acid is, of course, well known as a good protein precipitant. Acetic acid is a very weak acid (a 5 *N* acid solution yields a *p*H of only 2.3), but the peptization results fall on the

hydrochloric acid *p*H peptization curve. Phosphoric acid at 5 *N* concentration (*p*H 0.7) extracts more nitrogen from undialyzed cottonseed meal than any of the other acids in the measurable *p*H range. It must be remembered, however, that phosphoric acid is a weak acid; it cannot be expected to compare in concentration with hydrochloric, sulfuric, or trichloroacetic acids for obtaining a *p*H value of approximately 0.5.

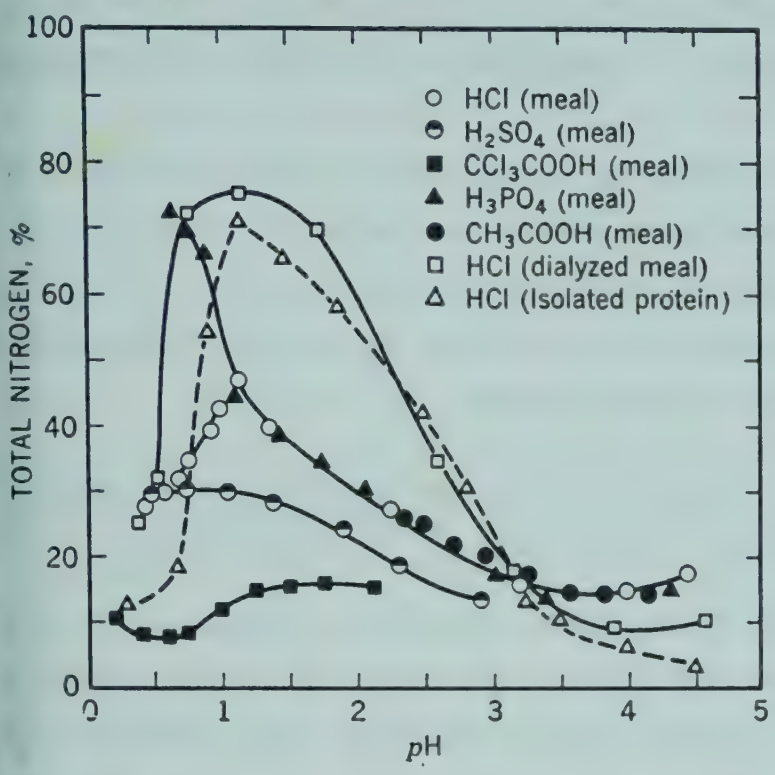


Fig. 101. Percentage of total nitrogen of solvent-extracted cottonseed meal and meal fractions peptized in acid solutions at different *p*H values.[68]

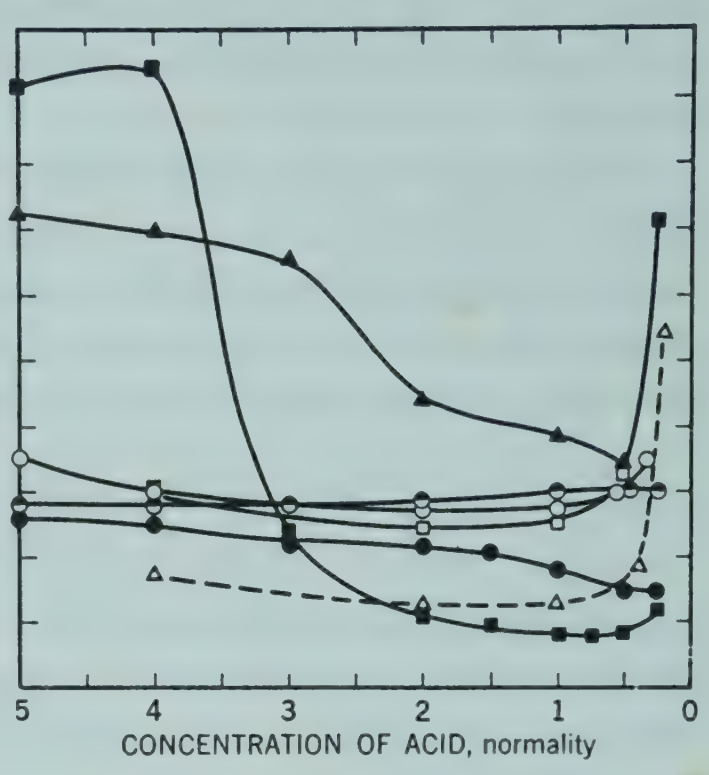


Fig. 102. Percentage of total nitrogen of solvent-extracted cottonseed meal and meal fractions peptized in strong acid solutions of different normalities.[68]

The proportionately greater peptization of the proteins of dialyzed cottonseed meal and isolated cottonseed protein (Fig. 101) in hydrochloric acid solutions, as compared with those of the undialyzed cottonseed meal, suggests that the presence of naturally occurring dialyzable meal constituents decreases the solubility of the meal proteins in acid solutions. This effect will be discussed in more detail later.

A relatively low concentration of the strong acids gives a *p*H value of 0.5. The effect of these acids on the solubility, or perhaps more accurately, on the precipitability of the cottonseed meal proteins at higher acid concentrations is shown in Figure 102. Data for the weaker acids have also been included in this figure, even though the highest acid concentration yields a measurable *p*H value. It is significant that there are no differences in the shapes of the hydrochloric acid peptization curves for the proteins of cottonseed meal, dialyzed cottonseed meal, and isolated cottonseed protein. Also, there is no appreciable difference between the actions of sulfuric and hydrochloric acids at concentrations greater than 1.0 *N*, both being equally good precipitating agents for cottonseed proteins.

The action of trichloroacetic acid on proteins is of theoretical importance because this acid is generally considered to be nearly specific for the quantitative precipitation of proteins. From the data shown in Figure 102 it is apparent that trichloroacetic acid is a good precipitant for the proteins of cottonseed only under certain limited conditions. A constant minimum protein solubility only occurs in the narrow normality range of 0.5 to 1.0 *N*. This concentration range is critical; an increase in acid to 4.0 *N* results in the peptization of approximately 95% of the meal nitrogen.

Although the solubility of the proteins of cottonseed meal in relatively high concentrations of strong and weak acids is of no particular significance in the extraction of the proteins, it indicates the nature of the action to be expected if the cottonseed proteins are to be used in commercial processes which require strong acid concentrations.

4. Solubility of Solvent-Extracted Cottonseed Meal Proteins and Isolated Cottonseed Globulin in Alkaline Solutions of Neutral Salts

In the commercial production of cottonseed protein, it would be desirable to be able to extract the proteins from the meal at a much lower *p*H than 10.0. The possibility of this has been suggested by a number of

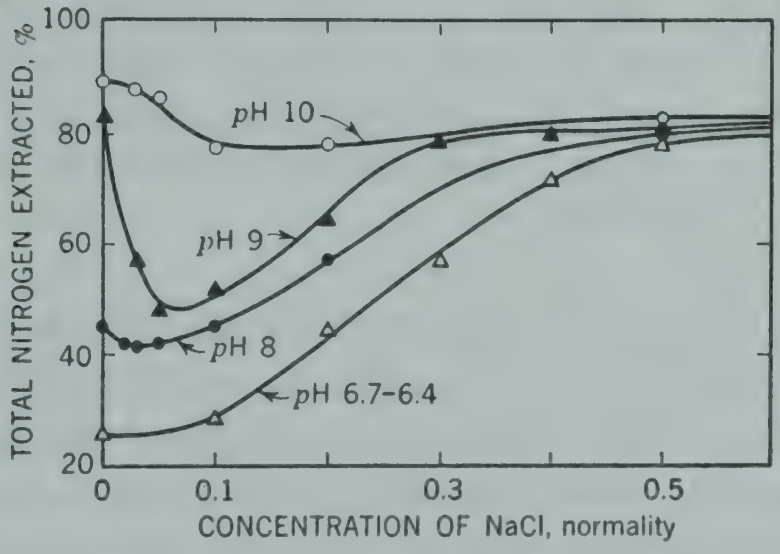


Fig. 103. Effect of sodium chloride concentration on extractability of proteins from cottonseed meal at different *p*H levels.[66] (NaOH used to bring the solutions to the *p*H values indicated.)

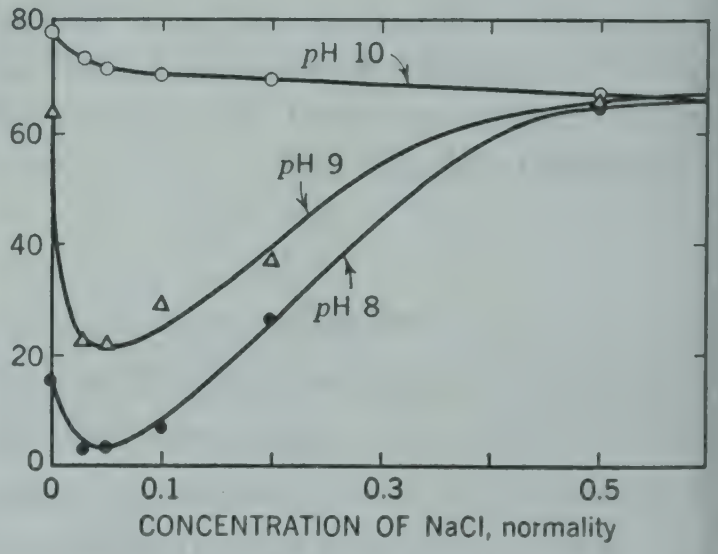


Fig. 104. Effect of sodium chloride concentration on the solubility of a cottonseed globulin preparation at different *p*H levels.[66]

investigators,[71] since they have found that protein solubility at constant *p*H on the alkaline side of the isoelectric point is markedly increased by the presence of salt at low or moderate concentrations. It appeared plausible that the globulin fraction of cottonseed meal might be extracted at lower *p*H values in the presence of low concentrations of salt. Experi-

[71] C. L. A. Schmidt, *The Chemistry of The Amino Acids and Proteins*, C. C Thomas, Springfield (Ill.), 2nd ed., 1944, pp. 940–941.

mentally, however, it was found[66] that at low salt concentrations the solubility of the cottonseed meal proteins is actually suppressed. That this behavior is not limited to cottonseed meal proteins was demonstrated by similar results on isolated cottonseed globulin and soybean globulin,[66] on soybean meal proteins and hempseed meal proteins,[66] and on peanut meal proteins.[70] While these results appear to be contrary to considerations of theoretical solubility with respect to globulins, they are of considerable importance from the standpoint of the commercial production of proteins from solvent-extracted cottonseed meal and other seed meals.

The influence of sodium chloride concentration on the extractability of cottonseed meal proteins at constant *p*H values is shown in Figure 103. At *p*H 10.0, the solubility of the glutelin fraction is suppressed completely at 0.1 *N* sodium chloride concentration, but the globulin fraction shows only a slight decrease in solubility. At *p*H 9.0, however, the solubility of the globulin fraction is decreased markedly by low salt concentrations, a maximum suppression of solubility equivalent to 50% of the globulin fraction occurring in sodium chloride solutions 0.05 to 0.07 *N*. At *p*H 8.0, the antagonistic effect of sodium chloride is only slight, but then, too, the solubility of the globulin is low at *p*H 8.0 in the absence of added salt. The lowest curve in Figure 103 shows the effect of sodium chloride on the solubility of the globulin fraction when the *p*H is not adjusted. The *p*H varied from 6.7 in the absence of added sodium chloride to 6.4 in 0.5 *N* sodium chloride solution.

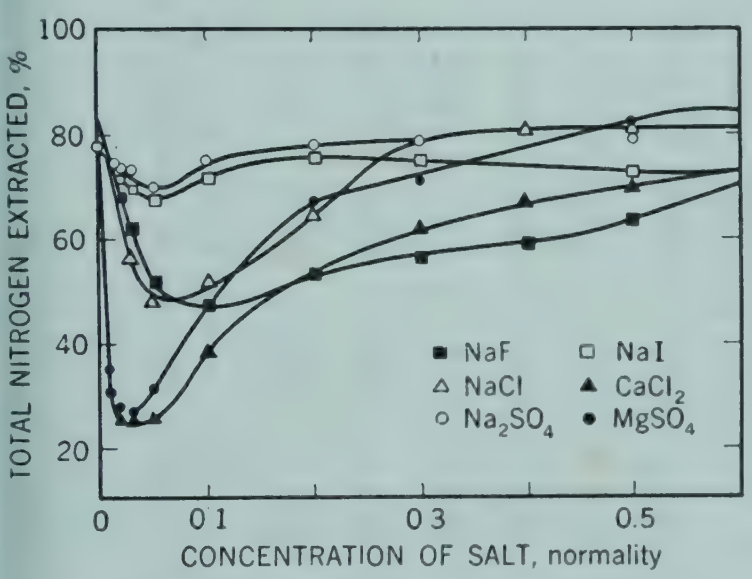


Fig. 105. Comparison of the effect of different inorganic salts on the extraction of protein from cottonseed meal at *p*H 9.0.[66]

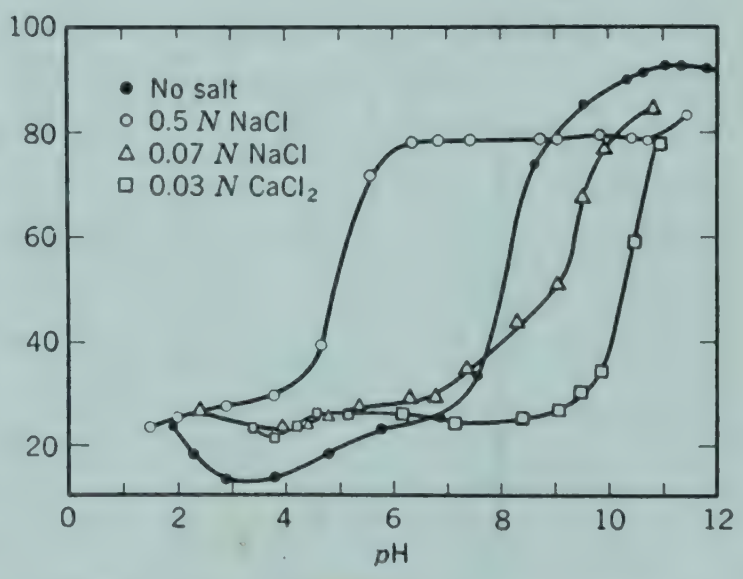


Fig. 106. Solubility of proteins of cottonseed meal in water and in weak solutions of NaCl and $CaCl_2$ at different *p*H levels.[66]

The solubility of isolated cottonseed globulin at *p*H values of 10.0, 9.0, and 8.0, in the presence of varying concentrations of sodium chloride,[66] is shown in Figure 104. The suppression of the isolated globulin's solubility by low concentrations of sodium chloride at *p*H 9.0 is slightly more pronounced than that observed for the cottonseed meal proteins.

TABLE 137

Extraction of Nitrogenous Substances from Solvent-Extracted Cottonseed with Various Salt Solutions[a, b]

Salt concn., normality	NaCl			KCl			Na_2SO_4			K_2SO_4			$MgSO_4$		
	NaOH, milli-equiv.	*p*H	N extd., %	NaOH, milli-equiv.	*p*H	N extd., %	NaOH, milli-equiv.	*p*H	N extd., %	NaOH, milli-equiv.	*p*H	N extd., %	NaOH, milli-equiv.	*p*H	N extd., %
0.0	1.35	9.00	83.6	1.40	8.95	77.4	1.40	8.95	77.4	1.40	8.95	77.4	1.45	9.00	83.6
0.01	—	—	—	1.41	8.88	71.4	1.51	8.92	74.1	1.41	8.90	74.8	1.55	8.95	30.8
0.02	—	—	—	1.45	8.88	58.8	1.56	9.00	73.5	1.45	8.93	71.6	1.60	8.90	28.2
0.03	1.40	9.10	57.3	1.47	8.90	57.6	1.61	9.00	73.3	1.47	8.88	68.6	1.65	8.92	27.2
0.05	1.45	9.05	48.7	1.51	8.88	50.5	1.66	8.97	69.5	1.51	8.90	67.2	1.75	8.90	31.8
0.10	1.52	8.95	52.0	1.55	8.85	52.8	1.75	9.05	75.6	1.55	8.90	67.2	1.90	8.88	47.2
0.20	1.62	8.90	65.2	1.60	8.85	62.3	1.82	9.05	78.5	1.60	8.88	75.5	2.05	8.90	67.5
0.30	1.65	8.95	79.6	1.61	8.95	74.2	—	—	—	1.61	9.00	76.0	2.20	8.95	71.5
0.40	1.66	8.88	80.5	1.62	8.95	75.4	—	—	—	1.62	9.00	76.3	—	—	—
0.50	1.67	8.90	81.5	1.63	8.82	75.5	1.90	9.00	79.0	1.63	8.85	76.0	2.25	8.92	82.8

[a] H. S. Olcott and T. D. Fontaine, *J. Am. Chem. Soc.*, **62**, 1334–1339 (1940).

[b] 5 g. of meal was extracted with 200 ml. of solution. Two separate batches of meal were used. *p*H adjusted by addition of sodium hydroxide.

Since proteins have a net negative charge on the alkaline side of their isoelectric points, the change in solubility of the proteins at alkaline *p*H values can be attributed to the interaction of the cation with the protein. While the cation has a precipitating effect on the protein, the anion of the salt has a peptizing tendency at alkaline *p*H values. The magnitude of the effects of both ions of a number of inorganic salts on the solubility of the cottonseed meal proteins at *p*H 9.0 is shown in Figure 105. In the case of the sodium salts, the importance of the anions is demonstrated. The sulfate and iodide ions have a much greater peptizing effect than do the chloride and fluoride ions. The results obtained for potassium chloride and sulfate (Table 137) are almost identical with those observed with the corresponding sodium salts. It is important to note that the amount of sodium hydroxide necessary to maintain a practically constant *p*H must be increased with increased salt concentration.

The effect of divalent cations on the protein solubility, as illustrated by calcium and magnesium, is much greater than that of the monovalent cations (Fig. 105). Solubility of the globulin fraction of cottonseed meal is almost completely suppressed at *p*H 9.0 in the presence of 0.03 to 0.05 *N* calcium chloride and magnesium sulfate solutions. With increasing salt concentration, the solubility of the globulin fraction increases.

To illustrate the effect of low concentrations of sodium chloride (0.07 *N*) and calcium chloride (0.03 *N*) on the extraction of proteins from the solvent-extracted cottonseed meal, typical *p*H–peptization curves are shown in Figure 106. Calcium chloride (0.03 *N*) completely suppresses the solubility of the globulin fraction at *p*H values below 9.0. Although sodium chloride (0.07 *N*) has a less pronounced effect than calcium chloride, the former decreases rather than increases the protein solubility at alkaline *p*H values. This is in contrast to the effect of 0.5 *N* sodium chloride on the normal *p*H–peptization curve for solvent-extracted cottonseed meal proteins (Fig. 100). These factors are of considerable importance from the standpoint of extracting cottonseed meal using *hard* waters, because even small amounts of calcium and magnesium significantly decrease the amount of protein extracted.

5. Effect of Phytic Acid on Solubility of Cottonseed Meal Proteins

Solvent-extracted cottonseed meal contains about 7 to 9% ash, consisting mainly of calcium, magnesium, potassium, and phosphorus. It may appear surprising, therefore, that the addition of small amounts of inorganic salts has such a pronounced effect on the protein solubility. Yet, after a thorough investigation, it has been found [5] that cottonseed meal and other seed meals contain phytic (inositol hexaphosphoric) acid which is capable of forming insoluble mixed salts with calcium, magnesium, and potassium at alkaline *p*H values, thus rendering the naturally occurring

cations unobtainable for forming insoluble protein-cation complexes. The ratio of phytic acid to total cations in the meal must be fairly well balanced, because, by the addition of small amounts of various salts, the combining power of the phytic acid is exceeded and the cations are free to enter into reaction with the protein. Phytic acid not only performs this essential function of rendering the natural meal cations unavailable at alkaline *p*H values, but also has a very marked influence on the solubility of the meal proteins at acid *p*H values below their isoelectric point. It should be borne in mind that, on the acid side of the isoelectric point, proteins have a net positive charge and are capable of combining with the anions of various salts and acids.

The solubility of solvent-extracted cottonseed meal proteins, dialyzed cottonseed meal proteins, and isolated cottonseed protein was determined [5] over a wide *p*H range, using hydrochloric acid and sodium hydroxide to adjust the *p*H (Fig. 107).

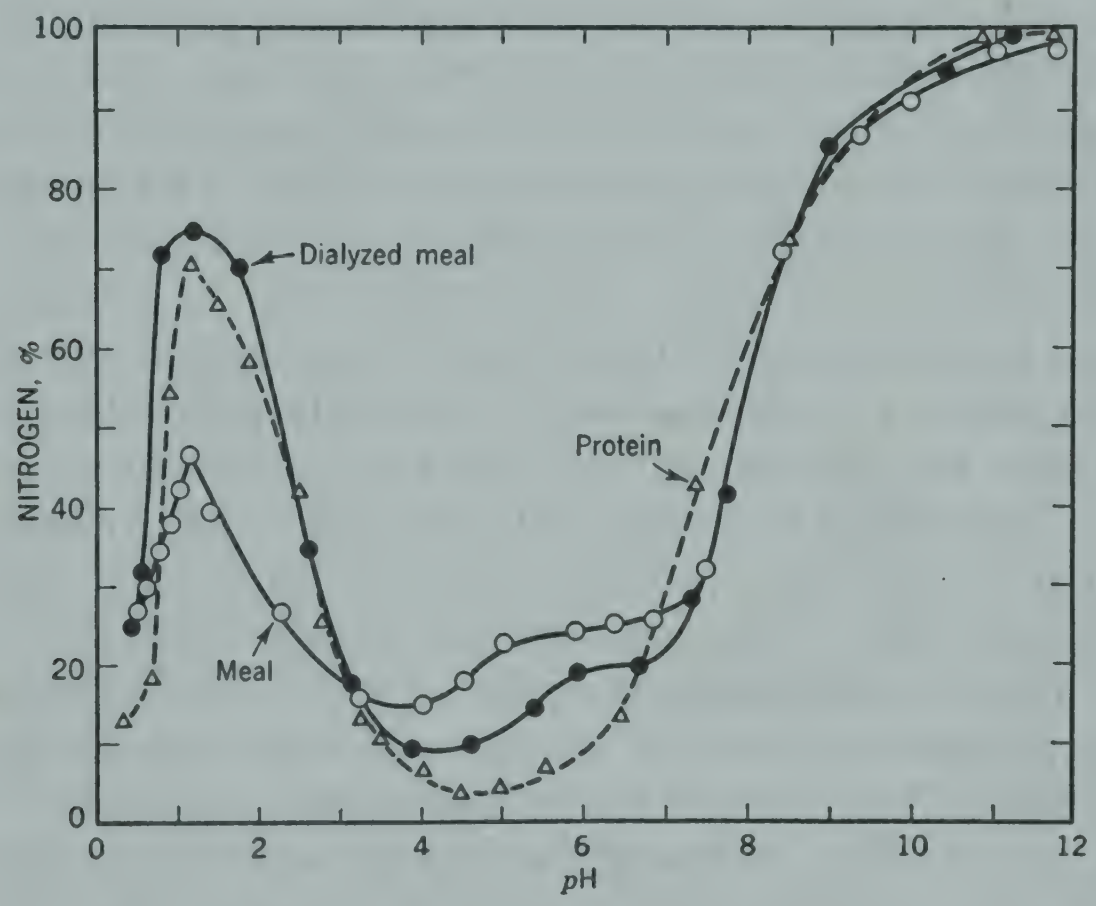


Fig. 107. Percentage of total nitrogen peptized in solvent-extracted cottonseed meal, dialyzed meal, and isolated cottonseed protein at different *p*H values.[68] (Hydrochloric acid and sodium hydroxide used for adjustment of the *p*H.)

The cottonseed meal was produced by ethyl ether extraction of the oil from cottonseed flakes and gave the following analysis: water, 11.5%; nitrogen, 8.21%; ash, 8.7%; and phosphorus, 1.53%. Subsequent batches of the same cottonseed flakes were extracted with (*a*) Skellysolve F (petroleum naphtha), (*b*) Skellysolve F followed by ethyl ether, and (*c*) ethyl ether followed by chloroform. The *p*H–peptization curve shown

in Figure 107 for the ethyl ether-extracted cottonseed meal is representative of all of the cottonseed meals, regardless of the solvent or combination of solvents used for removing the oil.

Dialysis of solvent-extracted cottonseed meal resulted in the loss of 33% of the meal solids, including 7% of the total meal nitrogen and 65% of the ash. The effect on the peptization of the cottonseed meal proteins of removing, by dialysis, 33% of the meal solids is quite marked in the acid region below *p*H 3.0, whereas there is little or no effect at alkaline *p*H values. The increased peptization of the proteins in the *p*H range 0.75 to 2.5 is due to the previous removal, by dialysis, of perhaps 65% of the total phytic acid.

The protein used in these investigations was isolated from an extract (*p*H 11.0) of solvent-extracted cottonseed meal by precipitation at *p*H 4.0 with hydrochloric acid. The moist protein precipitate was suspended in cellophane membranes and dialyzed with shaking against running distilled water for three days. The protein was dried by the lyophilization process [72] and gave the following analysis: water, 10.6%; nitrogen, 14.0%; ash, 0.22%; and phosphorus, 1.16%. It is evident that the isolated protein contains a relatively high percentage of phosphorus and, therefore, of phytic acid; nevertheless, the ratio of phosphorus to nitrogen in the cottonseed meal is much higher than in the isolated protein.

The isolated protein *p*H–peptization curve approximates the dialyzed meal curve very closely in the acid and alkaline *p*H ranges but differs slightly in the isoelectric zone. That the isolated protein shows higher solubility at acid *p*H values than the undialyzed meal proteins indicates that the ratio of phytic acid to protein is less in the isolated protein. Similar solubility results have also been obtained for solvent-extracted soybean and peanut meals, dialyzed peanut meal, and isolated peanut protein.[5]

Phytic acid is a major impurity in isolated seed meal proteins, but the amount present varies considerably, depending upon the method of isolation. In order to arrive at a clear understanding of the reason for these variations, the solubility of the phosphorus and nitrogen compounds in cottonseed meal extracts, as a function of *p*H, was determined (Fig. 108).

It is apparent that the solubility of the total phosphorus compounds does not correspond to that of the nitrogenous constituents. A minimum total phosphorus solubility (17% of the total phosphorus) occurs at approximately *p*H 2.75, whereas the minimum solubility range for the nitrogenous constituents extends from *p*H 2.0 to 7.0. Maximum total phosphorus solubility (85%) is obtained at *p*H 0.7 and 6.0; it is evident, however, that between *p*H 6.0 and 2.75 increasing amounts of phytic acid combine with the proteins even though the proteins are in an insoluble state. The net

[72] A. F. Pomes and G. W. Irving, Jr., *Science,* **101,** 22 (1945).

positive charge on the insoluble proteins increases over this *p*H range and accounts for the increased reaction between the phytic acid ion and the proteins.

From *p*H 6.0 to 7.0 there is a very sharp decrease in the amount of total phosphorus that is soluble. The decrease in phosphorus solubility is due to the formation of insoluble mixed calcium, magnesium, and potassium salts of phytic acid, rather than to interaction of protein and phytic acid. An almost constant phosphorus solubility value (30%) is obtained over the *p*H range 7.0 to 11.0.

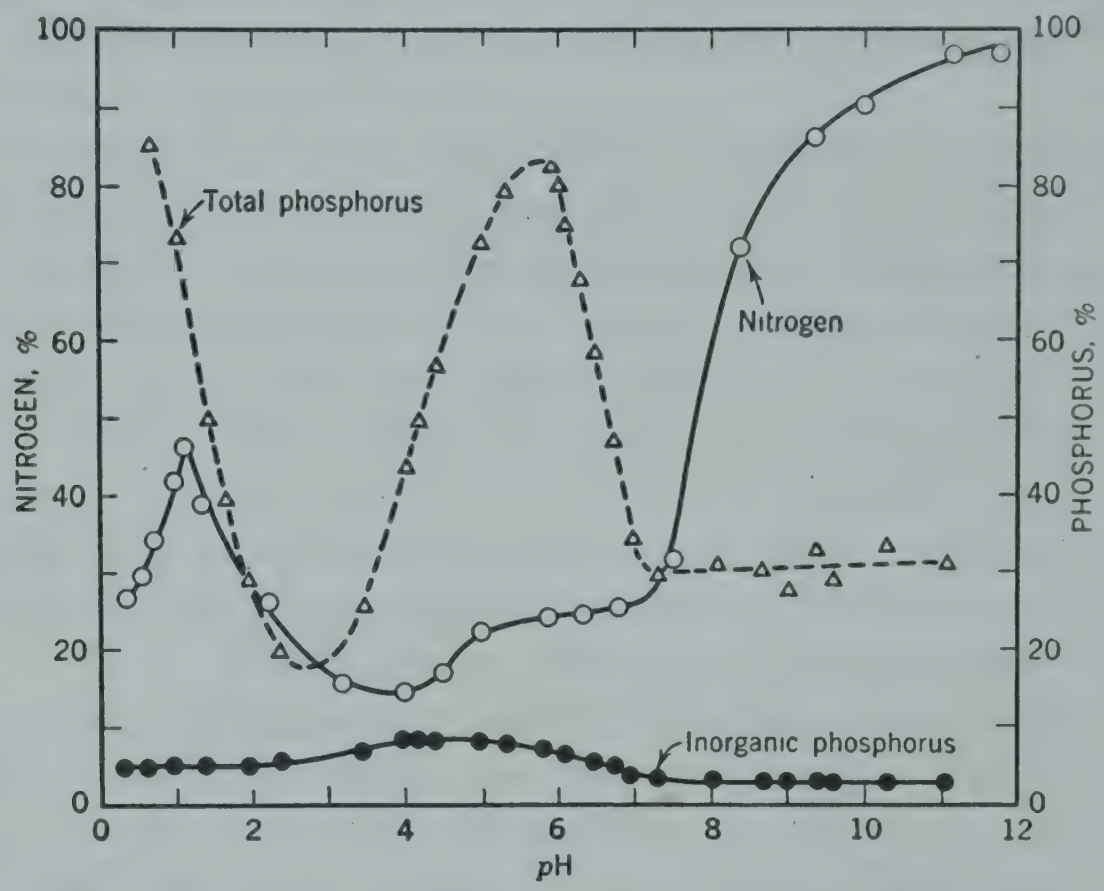


Fig. 108. Percentages of total nitrogen, total phosphorus, and inorganic phosphorus of solvent-extracted cottonseed meal which are soluble in solutions adjusted to different *p*H values with hydrochloric acid and sodium hydroxide.[5] (Values for inorganic phosphorus are in terms of percentages of total meal phosphorus.)

At *p*H values lower than 2.75 the total phosphorus solubility appears to coincide with the nitrogen solubility until *p*H 1.5 is reached. At still lower *p*H values the phosphorus solubility continues to increase; whereas the nitrogen solubility decreases. This effect is attributed to the fact that at low *p*H values the chloride ion begins to displace the phytic acid ion from the insoluble protein.

The inorganic phosphorus in the meal does not appear to enter into reaction with the protein in the presence of an excess of phytic acid phosphorus. The slight increase in the inorganic phosphorus content in the *p*H range 3.0 to 6.0 is caused by the action of a naturally occurring enzyme, phytase, which is capable of hydrolyzing phytic acid to yield inositol and phosphoric acid.

The solubility of the total phosphorus compounds of cottonseed meal in sulfuric and trichloroacetic acid solutions, as shown in Figure 109, is almost the same as in hydrochloric acid solutions. With the same acids, solubility behavior at *p*H values below the protein isoelectric range is in

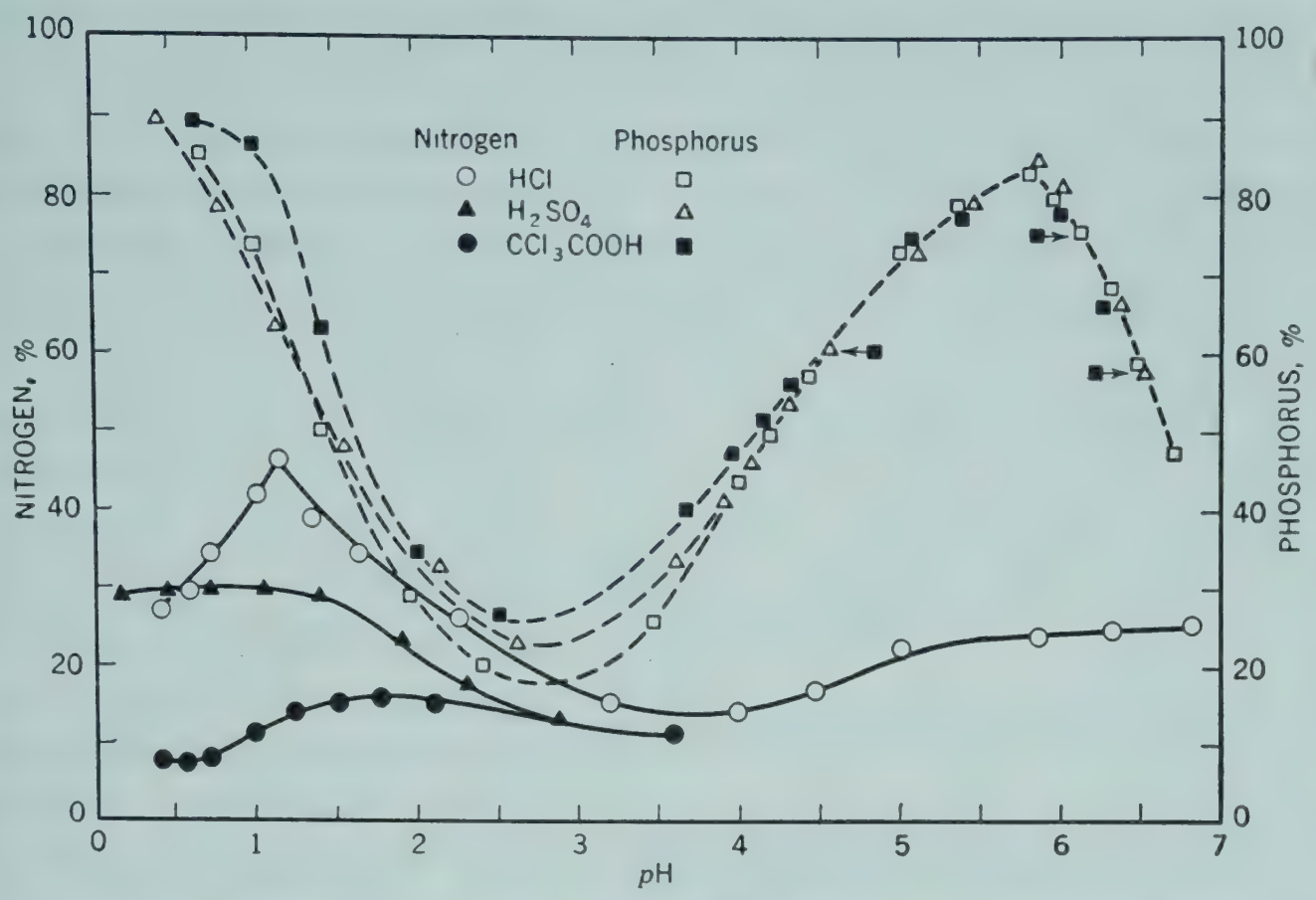


Fig. 109. Percentages of total nitrogen and total phosphorus of solvent-extracted cottonseed meal which are soluble in hydrochloric, sulfuric, and trichloroacetic acid solutions at different *p*H values.[5]

contrast to that observed in the case of peanut meal.[5] However, the inappreciable variation in solubility of the phosphorus compounds in cottonseed meal at *p*H values below the protein isoelectric range may be attributed to the fact that these acids differ less in their ability to peptize cottonseed meal proteins than in their ability to peptize peanut meal proteins at *p*H values below the isoelectric point.

For direct proof that phytic acid is responsible for the decreased protein solubility of undialyzed cottonseed meal proteins (as compared to dialyzed cottonseed meal proteins) at *p*H values below their isoelectric point, phosphorus, in the form of sodium phytate and phytic acid, was added to dialyzed cottonseed meal in the approximate amount that was lost on dialysis. The acid *p*H–peptization curve was then determined using hydrochloric acid to adjust the *p*H in all cases. The result shown in Figure 110 illustrate clearly that phytic acid, a normal constituent of cottonseed meal, is responsible for the decreased protein solubility of undialyzed cottonseed meal as compared to the dialyzed meal in the *p*H range 3.0 to 0.5. Actually, the amount of sodium phytate added (equivalent to 260 mg. per 2.5 g. of undialyzed meal) was in slight excess of that removed during dialysis, so the peptization curve is even lower than the

normal meal curve. The greater peptization of the proteins of dialyzed meal when phytic acid was added may be attributed to the fact that the phytic acid used was impure and contained only 22% phosphorus, of which one-fifth was inorganic phosphorus.

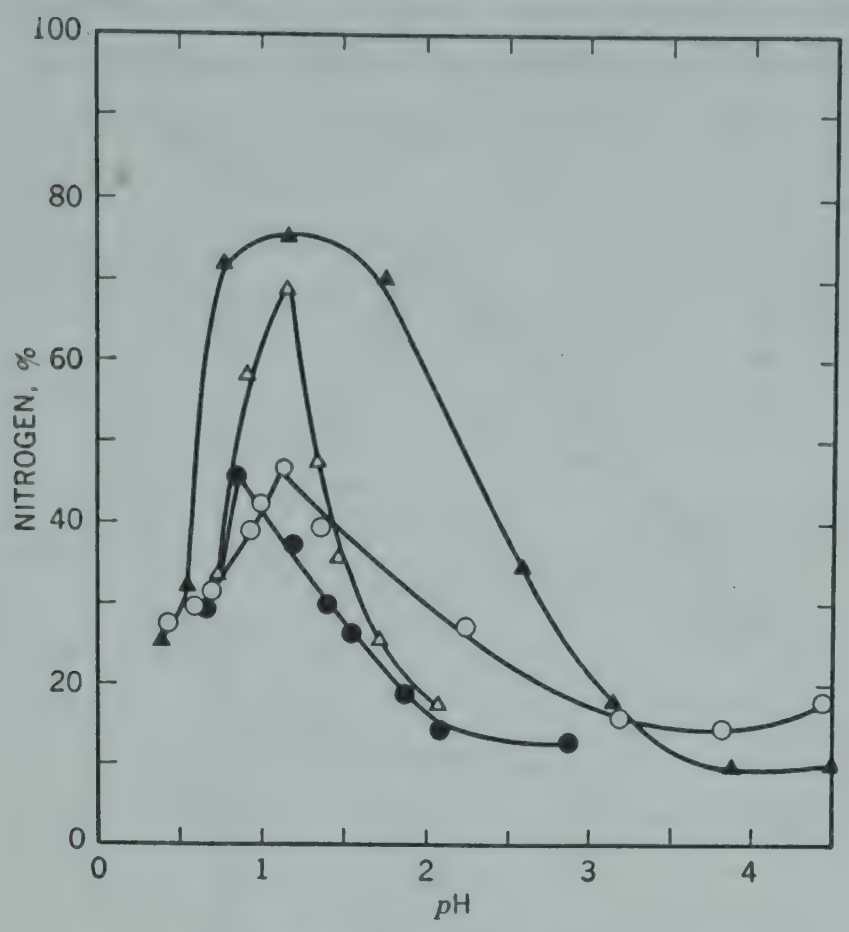


Fig. 110. Effect of phytic acid and sodium phytate on the solubility of the nitrogenous constituents of dialyzed and undialyzed cottonseed meal in hydrochloric acid solution at low *p*H values[5]: dialyzed meal, ▲; dialyzed meal plus phytic acid equivalent to amount of phosphorus lost in dialysis, △; dialyzed meal plus sodium phytate equivalent to the amount of phosphorus lost in dialysis, ●; undialyzed meal, ○.

The solubility of the phytic acid present in an isolated cottonseed protein fraction (page 456), containing 14.0% nitrogen, 0.22% ash, 1.16% total phosphorus, and 0.01% inorganic phosphorus, is shown in Figure 111. It is important to note that the isolated protein contained 0.22% ash and 1.16% phosphorus, as compared to the 8.7% ash and 1.53% phosphorus of the undialyzed cottonseed meal. The phosphorus solubility curve for the isolated protein differs from the corresponding solubility curve for undialyzed cottonseed meal (Fig. 108) in exhibiting a broader minimum solubility range, no decrease in the amount of soluble phosphorus at *p*H values above 6.0, and a significantly lower phosphorus solubility in the *p*H range just below the isoelectric zone of the protein. There are, likewise, certain similarities in the phosphorus solubility curves for the isolated protein and the meal: the phytic acid ion is displaced from the protein by the chloride ion at very low *p*H values, and, on the alkaline side of the isoelectric zone of the proteins, the protein–phytic acid complexes are increasingly dissociated. However, the shapes of the curves are different.

These factors are important from the standpoint of protein isolation. The protein used in the solubility investigation (Fig. 111) was extracted at *p*H 11.0 and precipitated at *p*H 4.0, and can represent, at most, about 80% of the total meal nitrogen (see Fig. 108). Under the conditions of extraction at *p*H 11.0, only about 30% of the phytic acid phosphorus remains in solution; therefore, only that amount can possibly react with the protein upon precipitation at *p*H 4.0. The percentage phosphorus in the isolated protein (after three days dialysis) was 1.16% or 11.6 mg.

phosphorus per gram of protein. It is apparent that the protein reacts almost completely with the phytic acid present in the original extract (*p*H 11.0) when precipitated at *p*H 4.0, and, furthermore, that the phytic acid is not removed from the protein by dialysis at *p*H 4.0. Although the maximum phytic acid combining power of the proteins of cottonseed meal occurs at *p*H 2.75, the preparation of this protein fraction demonstrates that even at *p*H 4.0 the proteins can combine with appreciable quantities of phytic acid. In order to prepare a protein containing less phosphorus from the *p*H 11.0 extract, it is necessary to precipitate the protein at the maximum phytic acid solubility range, *p*H 6.0 to 7.0 (Fig. 108).

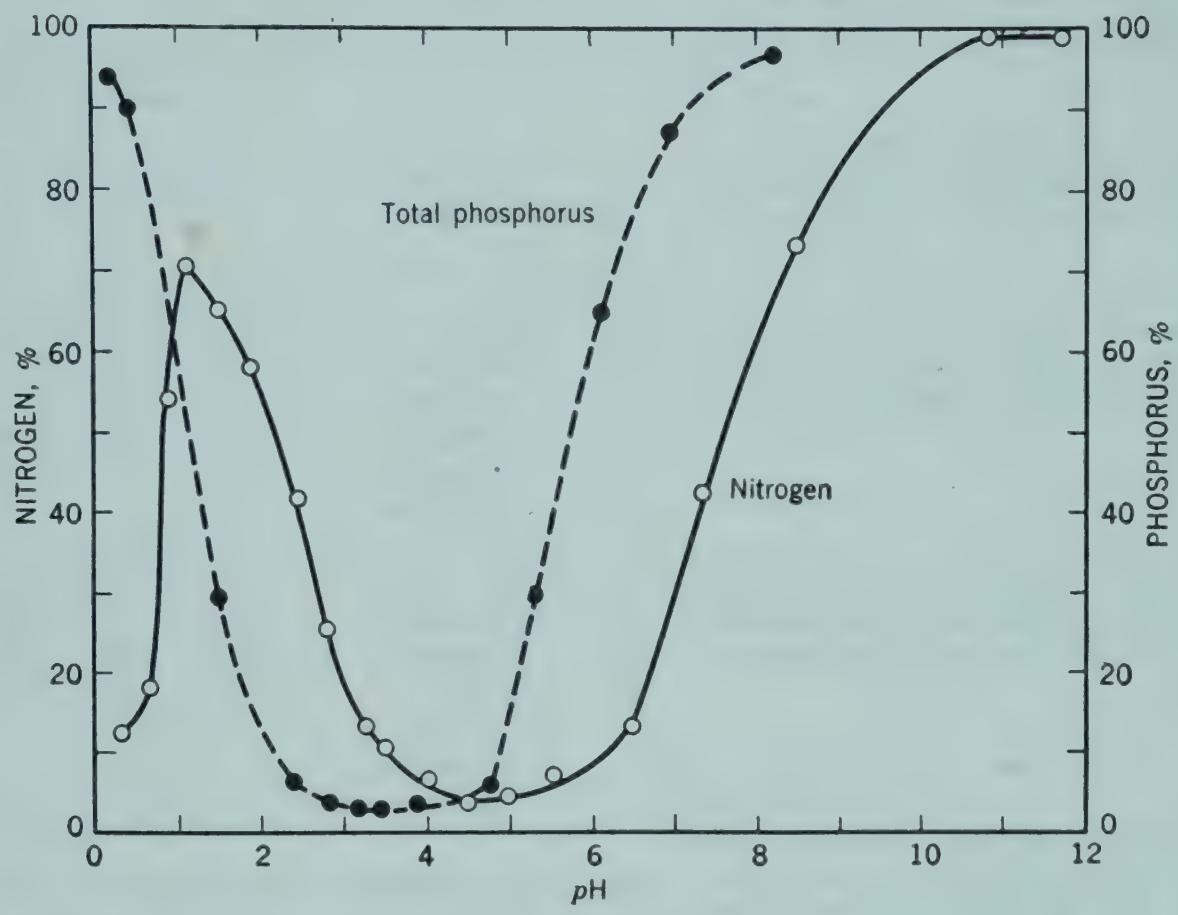


Fig. 111. Percentages of total nitrogen and total phosphorus of an isolated cottonseed protein which were soluble in a solution adjusted to different *p*H values with hydrochloric acid and sodium hydroxide.[5]

The effect of *p*H of extraction, precipitation, washing, and dialysis, and of organic solvents on the amount of phosphorus present in isolated cottonseed and peanut protein fractions is summarized in Table 138.[5] Most of this work has been done on peanut protein; however, similar results could be expected for cottonseed protein if investigations were conducted along the same lines. A number of important conclusions which can be drawn from this data are applicable to all seed meals. These are as follows: (*a*) the amount of phytic acid which will precipitate with a protein is dependent upon the *p*H of precipitation; (*b*) the phosphorus content of moist protein preparations is not decreased by washing of the moist protein with water (provided there is no appreciable change in *p*H)

TABLE 138

Nitrogen, Phosphorus, and Ash Content of Various Peanut and Cottonseed Protein Preparations[a]

Source and method of preparation[b]	Prepn. no.	Method of drying	Moisture, %	Ash, %	N, %	P, %
Red skinned peanuts. Protein extracted at *p*H 7.0 and precipitated at *p*H 6.0. Washed 3 times with water.	*1*	Alcohol-ether	10.2	0.2	15.3	0.21
	2	Air	10.5	0.2	14.9	0.24
The protein in the supernatant from nos. *1* and *2* was precipitated at *p*H 4.5. Washed 3 times with water.	*3*	Alcohol-ether	9.6	0.2	14.8	0.64
	4	Air	9.8	0.1	14.4	0.72
A portion of the *p*H 7.0 extract used for nos. *1* and *2* was adjusted to *p*H 4.5. Washed 3 times with water.	*5*	Alcohol-ether	9.4	0.2	15.0	0.52
	6	Air	9.3	0.3	14.9	0.70
Red skinned peanuts. Protein extracted at *p*H 8.2 and precipitated at *p*H 5.5. Protein was not water-washed.	*7*	Air	9.5	1.45	15.0	0.30
	8	Dioxane	9.7	1.71	14.8	0.30
	9	Acetone	8.8	1.15	15.3	0.35
	10	Methyl ethyl ketone	9.7	1.27	15.3	0.33
Red skinned peanuts. Protein extracted at *p*H 8.2 and precipitated at *p*H 4.5. Protein was not water-washed.	*11*	Air	9.3	1.33	14.2	0.85
	12	Dioxane	9.0	1.41	15.1	0.81
	13	Acetone	9.0	1.50	14.9	0.78
	14	Methyl ethyl ketone	8.9	1.48	15.0	0.79
White skinned peanuts. Protein extracted at *p*H 8.0 and precipitated at *p*H 4.5. Protein dialyzed for 72 hrs.	*15*	Lyophilized	10.4	0.31	15.4	0.64
Petroleum ether-extracted cottonseed. Protein extracted at *p*H 11.0 and precipitated at *p*H 4.0. Protein was not water-washed.	*16*	Air	9.3	3.35	13.0	1.14
	17	Dioxane	8.7	2.15	13.4	1.16
	18	Acetone	8.9	2.43	14.0	1.28
Ethyl ether-extracted cottonseed. Protein extracted at *p*H 11.0 and precipitated at *p*H 4.0. Protein dialyzed for 72 hrs.	*19*	Lyophilized	10.6	0.22	14.0	1.16

[a] T. D. Fontaine, W. A. Pons, Jr., and G. W. Irving, Jr., *J. Biol. Chem.*, **164**, 487–507 (1940).

[b] A single batch of protein was prepared for each group and the moist protein cake was divided into approximately equal parts. These were then dried as indicated.

or with organic solvent; (*c*) the phosphorus content is independent of the ash content; and (*d*) dialysis of aqueous suspensions of protein preparations will remove inorganic ash, but does not result in the removal of the phytic acid phosphorus, provided the *p*H of the dialyzing solution is not

adjusted to a value favorable to the dissociation of the protein–phytic acid complex.

From a theoretical standpoint, these results indicate a possible reason for the difficulty encountered in the purification of seed meal proteins, and in obtaining protein preparations having reproducible chemical and physical characteristics. In the preparation of protein from cottonseed meal, it appears advisable to water-wash the meal at *p*H 6.0, thus removing about 85% of the meal phosphorus and only a small amount of precipitable protein. Proteins prepared from water-washed cottonseed meal may have sufficiently desirable properties to warrant this step in the isolation procedure. Then, too, the water-wash can be used to recover by-products, such as phytic acid, which is a good source of biologically active inositol (cyclohexanehexol).

B. Hydraulic- and Expeller-Pressed Cottonseed Meals

The foregoing section has dealt almost entirely with the solubility characteristics of the nitrogenous constituents of solvent-extracted cottonseed meal. It was indicated in Tables 135 and 136 and in Figure 100, however, that commercial hydraulic-pressed cottonseed meal proteins are less soluble than those of solvent-extracted meal under the same extraction conditions. This factor alone prevents the recovery of any large amount of the protein from the hydraulic-pressed meal examined or from other meals that have been subjected to an elevated temperature and high relative humidity.

Since the industrial process of cooking cottonseed is more or less an art, the solubility characteristics of the nitrogenous constituents of a single meal previously mentioned can hardly be representative of the entire industry. Furthermore, the determination of complete solubility curves for a large number of meals would hardly be practicable. For this reason, in the work to be described here [26] the solubility of the nitrogenous constituents in 3% sodium chloride solution and in water was adopted as a test whereby comparative results might be obtained. The solubility in 3% sodium chloride solution reflects changes in the globulin protein fraction due to processing, while the solubility in water shows only the effect of prior treatment of the meal on the minor protein fraction. Under these conditions, the nitrogen solubility of various cottonseed meal samples in 3% sodium chloride was found to vary with the severity of heating and also with the length of heating.

Samples of commercial cottonseed meals obtained from fourteen different localities were subjected to solubility measurements as described above; the results are given in Table 139. The solubility of the nitrogenous constituents of ethyl ether-extracted cottonseed meal is also listed to show the magnitude of the differences between the solubility of the commercial

meal proteins and the solvent-extracted products. As would be expected, the water-soluble nitrogen of the various commercial meals does not vary appreciably; however, the solubility of the nitrogenous constituents in 3% sodium chloride varies from 46.7 to 9.6%. On the basis of these results, it appears that the average cooking conditions employed by a number of mills produce a meal from which only about 35% of the total nitrogen can be extracted with 3% sodium chloride solution, as compared to 75 to 80% from solvent-extracted meal.

TABLE 139

Comparison of the Solubilities in 3% Sodium Chloride and in Water of the Nitrogen Compounds in Commercial Cottonseed Meals from Different Localities[a]

Meal	Locality	Protein content (N × 6.18), %	Percentage of total nitrogen soluble	
			In 3% NaCl	In water
A	Phoenix, Ariz.	45.2	46.7	7.8
B	San Joaquin, Calif.	43.6	45.3	8.4
C	Lubbock, Texas	44.6	42.7	8.3
D	Memphis, Tenn.	46.7	38.0	6.7
E	Raleigh, N. C.[b]	40.6	35.8	5.9
F	Columbia, S. C.	43.8	35.2	7.3
G	Ft. Worth, Texas	44.4	34.7	9.2
H	Birmingham, Ala.	42.0	34.4	6.3
I	Montgomery, Ala.[b]	40.9	34.0	6.1
J	Atlanta, Ga.[b]	40.6	33.0	5.9
K	Charlotte, S. C.[b]	40.6	31.9	6.0
L	Augusta, Ga.[b]	40.5	30.0	6.6
M	Augusta, Ga.[b]	40.0	27.2	5.9
N	Macon, Ga.	40.1	22.0	7.5
O	Jackson, Miss.	42.1	9.6	7.1
	Ether-extracted cottonseed meal	50–52	75–80	20–30

[a] H. S. Olcott and T. D. Fontaine, *Ind. Eng. Chem.*, **34**, 714–716 (1942).
[b] All samples sieved (20-mesh screen) except these.

The degree of protein solubility is indicative of the degree of heat treatment employed in the production of the particular meal. The nutritive value of the meals is decreased in accordance with the decreased protein solubility, as measured by 3% sodium chloride extraction. When rats were fed commercial cottonseed meals *B*, *D*, *N*, and *O*, listed in Table 139, and ethyl ether-extracted cottonseed meal,[26] each at a 13% protein level in an otherwise complete diet, they showed an average weight gain, per gram of protein consumed of 1.71, 1.39, 1.24, 1.12, and 1.99 g., respectively. These results were obtained with a relatively small number of experimental animals, but the general order of results appears to be in line with results obtained by feeding ethyl ether-extracted cottonseed meal that had been autoclaved for various periods of time.[27]

In order to determine experimentally the change of solubility of the nitrogenous constituents of cottonseed with heat treatment, ground cottonseed meats (not flakes) were spread in thin layers and heated in a steam autoclave at 100% relative humidity for varying lengths of time and at temperatures ranging from 100° to 120° C. (212° to 248° F). The oil was removed with ethyl ether, and the oil-free autoclaved meal was tested for protein solubility using 3% sodium chloride solution. The results shown in Figure 112 indicate the progressive change in the solubility of the nitrogenous constituents under definite experimental conditions under which only temperature and time are variables. The methods of commercial cooking differ from those described above in many respects, such as the use of thin-flaked cottonseed, agitation during cooking, different heat treatments in successive stacks, and varying humidity conditions. All of these factors are important from the standpoint of detoxification of cottonseed meal, but for effective detoxification it is not necessary to subject cottonseed to conditions as extreme as is indicated by the results for some of the meals listed in Table 139.

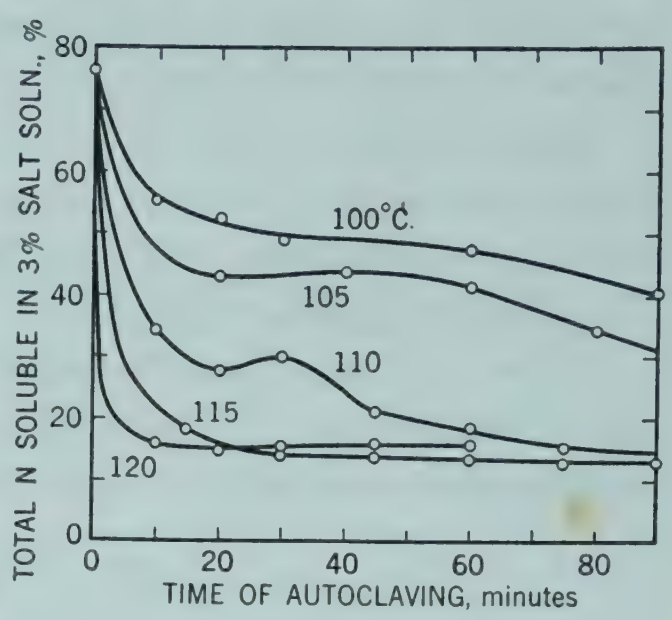


Fig. 112. Effect of autoclaving at different temperatures on solubility of nitrogenous constituents of cottonseed kernels in 3% sodium chloride solution.[26] (Autoclaved meats were extracted with ether prior to extraction with salt solution.)

On the basis of the nitrogen solubility results obtained on cottonseed meal *N* (Table 139), it can be concluded that the flaked cottonseed was subjected to rather high temperatures during the cooking process. Since cottonseed meal *N* was produced by the pressure-cooking method described by University of Tennessee investigators,[73] it is known that the cottonseed flakes were subjected to a relatively high temperature for a short period of time. Meal *O* must have received the most severe cook of any of the meals analyzed, since it gave the lowest nitrogen solubility results in 3% sodium chloride solution and the lowest nutritive value. It is not known whether cottonseed meal *O* was produced by the same general method employed for meal *N*, but high-temperature cooking conditions appear to be not uncommon in commercial practice. This phase of processing warrants further investigation if more nutritive and usable cottonseed meal is to be produced by existing methods. From the standpoint of protein solubility, at least, it is better, as suggested by Thornton,[74] to cook

[73] R. B. Taylor, *Chem. & Met. Eng.*, **44**, 478–481 (1937).
[74] M. K. Thornton, Jr., *Cottonseed Products*, Oil Mill Gazetteer, Wharton, Texas, 1932.

for longer periods and at relatively lower temperatures than at elevated temperatures for only a short time.

V. Industrial Application of Cottonseed Proteins

The suitability of a protein for industrial use depends not only upon its having desirable solubility properties, but also upon its color, viscosity characteristics, tackiness, and adhesive strength. The relative importance of these properties in the production of artificial protein fibers, films, flexible glues, cold water paints, paper coating adhesives, plywood glues, and related products will vary depending on the particular application. The color of isolated cottonseed proteins as compared to peanut and soybean proteins has been investigated to a limited extent.[75] Some data are also available on the viscosity characteristics of cottonseed protein as compared to peanut and soybean proteins.[76]

A. Color of Protein Preparations

The lack of appreciable color in a protein is not only advantageous, but is also frequently a prerequisite to its successful application to a particular industrial use. With the advent of better optical instruments, such as the photoelectric spectrophotometer, it has been possible to adapt the trichromatic system of the International Commission on Illumination to the evaluation of the color of various protein preparations.[75] Color evaluation and comparison are based on the color of 100 mg. of protein dissolved in 25 ml. of 0.02 *N* sodium hydroxide solution. For a proper evaluation, the protein solution must be clear and, in general, this is accomplished by centrifugation if the solution shows a faint turbidity. In some cases with cottonseed and soybean proteins, however, it is difficult to obtain clear solutions.

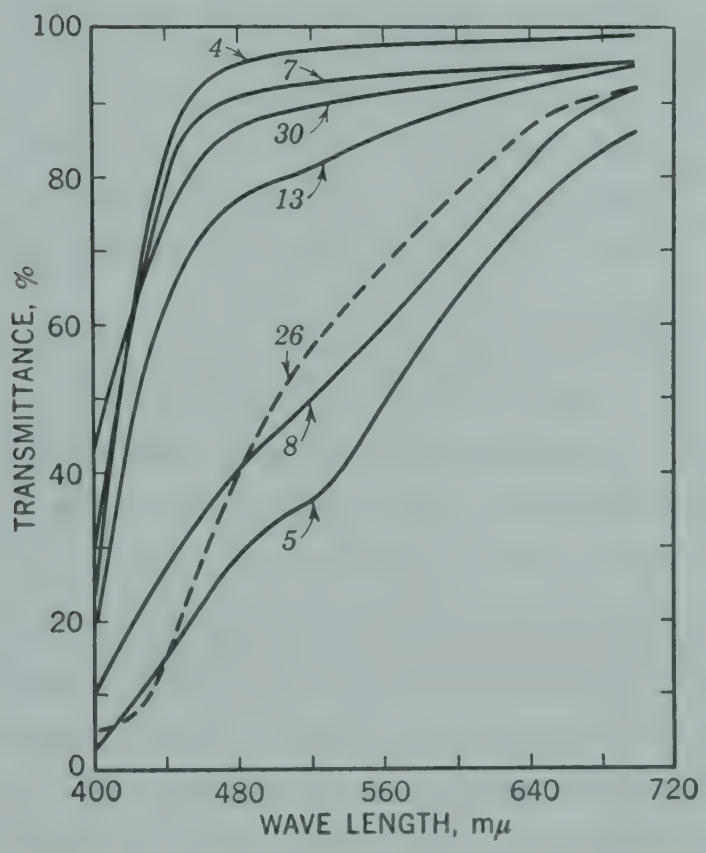


Fig. 113. Spectral transmittance curves for alkaline solutions of peanut, cottonseed, and soybean proteins: peanut proteins, *4, 5, 7, 8, 13;* cottonseed protein, *26*; soybean protein, *30*.[75]

The particular advantage of the method employed is that certain numerical values may be assigned to the color of the protein solution.

[75] T. D. Fontaine, S. B. Detwiler, Jr., and G. W. Irving, Jr., *Ind. Eng. Chem.*, **37**, 1232–1236 (1945).

[76] R. S. Burnett, E. J. Roberts, and E. D. Parker, *Ind. Eng. Chem.*, **37**, 276–281 (1945).

Thus, from the spectral transmittance data for cottonseed, peanut, and soybean protein solutions (as illustrated in Fig. 113), it is possible, by means of I.C.I. tristimulus values,[77, 78] to convert the transmittance values to the trichromatic coefficients, x, y, and z. In order to aid in the interpretation of results, the trichromatic data may, in turn, be converted to the psychophysical values of luminous transmittance, dominant wave length, and purity.[79, 80]

TABLE 140

Isolation of Cottonseed Protein Preparations for Colorimetric Investigation[a]

Protein no.	Meal used[b]	Extraction		Precipitation		Drying, washing agents
		Agent	*p*H	Agent	*p*H	
25	EE	NaOH	11.0	HCl	7.0	Air, 25°C.
26	EE	NaOH	11.0	HCl	4.0	Air, 25°C.
27	PE	NaOH	11.0	HCl	4.0	Air, 25°C.
27A	PE	NaOH	11.0	HCl	4.0	Dioxane
27B	PE	NaOH	11.0	HCl	4.0	Acetone
28	EE	0.5 *N*, NaCl	6.3	HCl	4.0	Air, 25°C.
28A	EE	0.5 *N*, NaCl	6.3	HCl	4.0	Dioxane
28B	EE	0.5 *N*, NaCl	6.3	HCl	4.0	Methyl ethyl ketone
28C	EE	0.5 *N*, NaCl	6.3	HCl	4.0	Acetone
29	PE	0.5 *N*, NaCl	6.3	HCl	4.0	Air, 25°C.
29A	PE	0.5 *N*, NaCl	6.3	HCl	4.0	Dioxane
29B	PE	0.5 *N*, NaCl	6.3	HCl	4.0	Methyl ethyl ketone
29C	PE	0.5 *N*, NaCl	6.3	HCl	4.0	Acetone

[a] T. D. Fontaine, S. B. Detwiler, Jr., and G. W. Irving, Jr., *Ind. Eng. Chem.*, **37,** 1232–1236 (1945).

[b] PE denotes petroleum ether (Skellysolve F or B)-extracted flakes; EE, ethyl ether-extracted flakes.

Cottonseed, peanut, and soybean proteins were analyzed colorimetrically by this method by Fontaine *et al.*[75] The methods used in preparation of the cottonseed proteins used in the investigation are shown in Table 140. It may be observed that an attempt was made to remove the pigments from the precipitated cottonseed proteins by washing the moist protein cakes with various organic solvents and that similar efforts were made to improve the color of peanut proteins. The soybean proteins were commercial samples and were analyzed without further treatment. The results of these investigations are shown in Figure 114 where the trichromatic coefficient values for x and y have been plotted and the psychophysical values, dominant wave length, and purity, have been superimposed on the

[77] A. C. Hardy, *Handbook of Colorimetry,* Technology Press, Cambridge, 1936.

[78] D. B. Judd, *J. Optical Soc. Am.,* **23,** 359–374 (1933).

[79] S. M. Newhall, D. Nickerson, and D. B. Judd, *J. Optical Soc. Am.,* **33,** 385–418 (1943).

[80] Optical Society of America, Colorimetry Committee, *J. Optical Soc. Am.,* **33,** 544–554 (1943).

plot. Since there may be some confusion concerning the use of the term "purity," it may be stated here that, the *lower* the colorimetric purity of the protein solution, and the nearer its x–y plot approaches the x–y plot for illuminant C, the *less* color it has. Luminous transmittance values for all the proteins shown in Figure 114 are in the original publication.

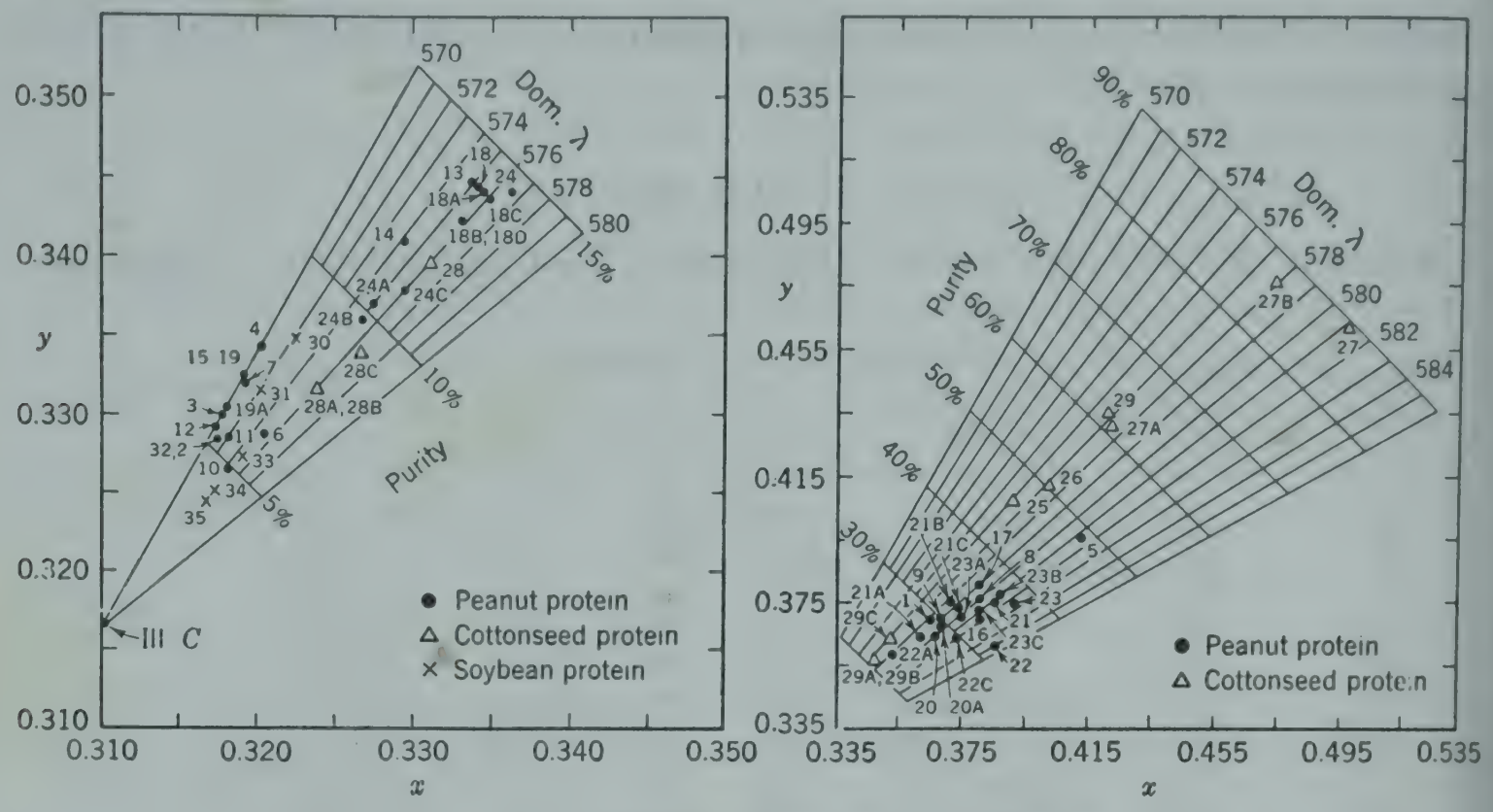


Fig. 114. Chromaticity diagram for alkaline solutions of peanut, cottonseed, and soybean proteins.[75] (The lower the colorimetric purity of the solution, and the nearer its x-y plot approaches the plot for illuminant C, the less color it has.)

There are several points to be considered in the interpretation of the color results on cottonseed proteins prepared from ethyl ether- and petroleum ether-extracted cottonseed meal, namely: (*a*) The ethyl ether meal contains less pigments than the petroleum ether meal, since only a very small fraction of the coloring matter of cottonseed is removed with the oil when petroleum ether is used. (*b*) The pigments may react with the proteins at *p*H 11.0, in alkaline extraction, whereas with sodium chloride extracts at *p*H 6.3 the pigments are less likely to react, but are occluded by the protein upon precipitation. (*c*) Dioxane and methyl ethyl ketone are better pigment solvents than is acetone. Thus, when the colors of the proteins prepared from the two meals by sodium hydroxide and sodium chloride extraction are compared, the sodium chloride- extracted protein is seen to contain much less color. The solvents were very effective in removing color from the proteins prepared from petroleum ether-extracted cottonseed meal by sodium chloride extraction (see nos. *29*, *29A*, *29B* and *29C* in Table 140), but in no case does the color of these proteins equal the color of proteins prepared by the same method from ethyl ether-extracted meal. In general, the color of the cottonseed proteins is inferior

to that of peanut proteins produced from white skinned peanuts and to that of the commercially produced soybean proteins.

B. Viscosity Characteristics

Viscosity characteristics of protein solutions vary considerably, depending upon the protein concentration, temperature, and *p*H of the solution. A major factor to be considered in using proteins for glues and adhesives is that their solutions must have a sufficiently long working life, that is, the viscosity of the solution must remain fairly constant for a

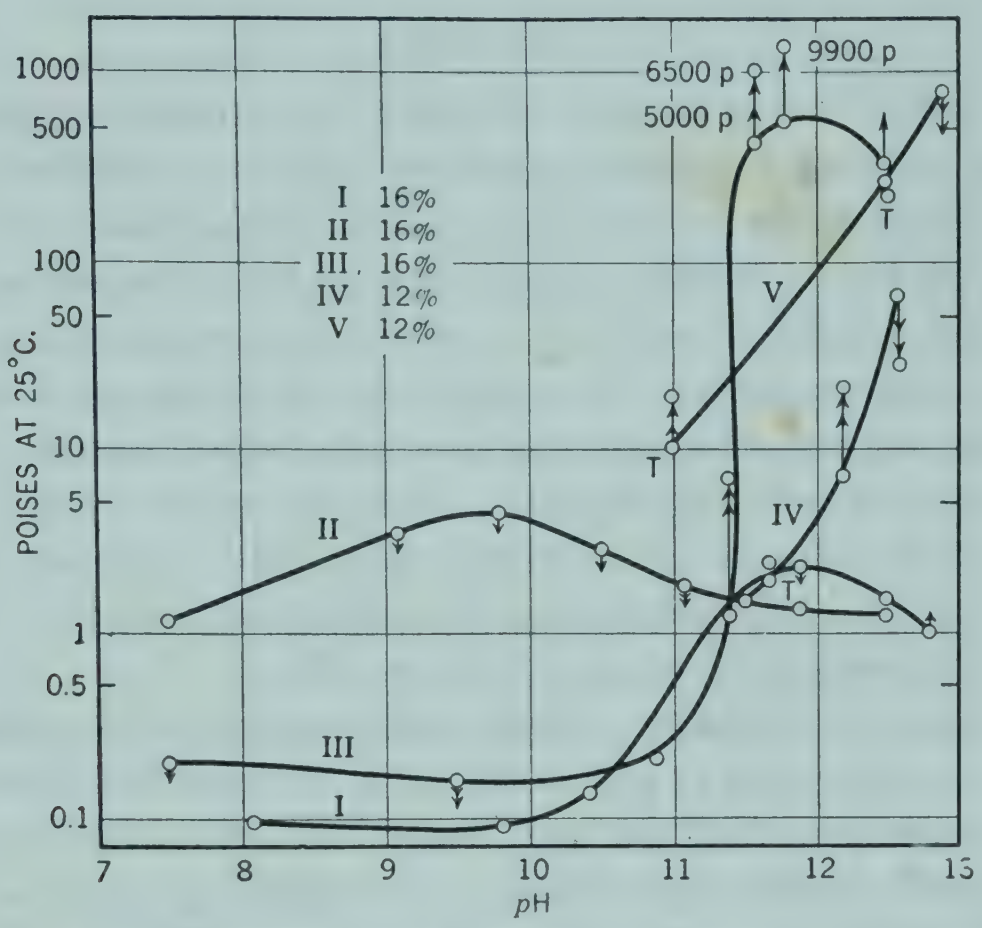


Fig. 115. Viscosity–*p*H curves for peanut (I), cottonseed (IV, V), and soybean (III) proteins extracted under mild conditions, and for a commercial soybean protein (II). T indicates that the solution is thixotropic. Arrows on the curves indicate change in viscosity at hourly intervals. Absence of arrows means no change in viscosity during the two-hour period of observation. One arrow at a point usually indicates that no change occurred after the first hour in the viscometer, although in some instances the viscosity was found to be constant during the first hour but to have undergone a change during the second hour.[76]

reasonable length of time. An increase in viscosity usually results in gelation or other undesirable flow properties, whereas a decrease in viscosity indicates possible hydrolysis and may result in loss of adhesive properties.

For adhesives, a relatively high protein concentration at a relatively low alkaline *p*H is desirable. It has been found that proteins which have received a mild hydrolytic treatment give the most desirable working properties. A good example of the difficulty that may be encountered, if native protein is used in preparing relatively concentrated protein solutions, is illustrated by the *p*H–viscosity curves for cottonseed, soybean,

and peanut proteins shown in Figure 115.[76] The particular cottonseed protein used in this investigation is seen to exhibit less desirable viscosity properties than the peanut protein, in that the solubility of the cottonseed protein is less at the lower *p*H values and that gelation occurs as soon as the solubility and viscosity increase. On the other hand, this figure illustrates the rather uniform viscosity characteristics exhibited by a commercial soybean protein over a wide *p*H range. There has been no reported work on the modification of cottonseed protein for specific uses, but much work has been done on other proteins which may be applicable.

C. Patents

Specific United States patents covering the preparation of cottonseed proteins from solvent-extracted cottonseed meal are limited to three in number.[81-83] These three are assigned to the Cotton Research Foundation and are based on the extraction of protein from unheated solvent-extracted cottonseed meal which has received a preliminary water-wash. The water-wash removes approximately 20 to 30% of the total meal nitrogen and an appreciable amount of nonnitrogenous meal constituents.

Nickerson [81] extracts the proteins from the water-washed meal with sodium hydroxide solution at relatively high *p*H values and precipitates the protein from the clarified extract by adjusting the *p*H of the solution with acid to the isoelectric range of the proteins.

Extraction of the globulin protein fraction with 3% sodium chloride solution and precipitation at *p*H 3.9 to 4.2 is claimed by Olcott.[82]

A later patent issued to Bass and Olcott [83] describes the use of a specific substance, gaseous carbon dioxide, as a precipitating agent for cottonseed proteins from an alkaline extract, to prevent overacidification.

There are obvious advantages and disadvantages in these methods of protein preparation. The object of the preliminary water-wash of the solvent-extracted cottonseed meal is to remove impurities. If the meal is not water-washed, considerably more difficulty is encountered in the handling of the precipitated protein. Even after the removal of the water-soluble materials, the cottonseed proteins have a tendency to form slimy precipitates which neither centrifuge nor filter well. The high alkalinity of extraction employed by Nickerson [81] is necessary if the major portion of the protein (globulin plus glutelin) is to be removed, but this is not conducive to obtaining proteins of low color.[75] The sodium chloride extraction method of Olcott [82] produces a protein fraction having more uniform characteristics and lighter color than the alkaline extraction method, but an appreciable loss of protein may be encountered in the precipitation

[81] R. F. Nickerson (to Cotton Research Foundation), U.S. Pat. 2,194,835 (1940).
[82] H. S. Olcott (to Cotton Research Foundation), U.S. Pat. 2,194,867 (1940).
[83] L. W. Bass and H. S. Olcott (to Cotton Research Foundation), U.S. Pat. 2,326,195 (1943).

step. Carbon dioxide as a protein precipitant [83] is unique in that it causes less denaturation than other acids, but in the recovery of the protein by centrifugation methods the excess carbon dioxide is apt to be thrown out of solution. Since sodium carbonate is formed in the neutralization of sodium hydroxide with carbon dioxide, the removal of the excess carbon dioxide by centrifugation causes an increase in *p*H of the solution and the protein tends to redissolve. Removal of the protein by filtration might result in better recovery of protein. These examples of the factors that must be considered in the preparation of cottonseed protein indicate that improvement in the process of extraction and precipitation may be necessary before the successful commercial production of cottonseed protein can be accomplished.

From the commercial standpoint it should be borne in mind that only from solvent-extracted cottonseed meal is there any indication that the preparation of protein will be successful. On a competitive basis with other proteins, it is questionable whether cottonseed protein will eventually compete for a market unless it is proved to have superior qualities. If solvent-extracted meal should sell at $40.00 per ton, the cost of a pound of isolated protein would not be less than $0.07 on the basis of meal cost alone. Cottonseed meal will undoubtedly continue as a major source of high protein feed whether it is produced by mechanical or solvent extraction methods, but the extent of its application for industrial uses will depend upon further research and engineering developments.

CHAPTER IX

MISCELLANEOUS CONSTITUENTS

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I. Introduction

For purposes of discussing its miscellaneous constituents, the cottonseed may be considered to comprise three parts, namely, linters, hulls, and kernels. On the outside of the seed, after removal of the lint by ginning, there remains a fuzzy coating of short fibers known as linters. The linters are removed from the seed at the oil mills immediately before the seed is processed for oil and meal. Upland cottonseed, which is the type most commonly grown in the United States, ordinarily yields about 200 pounds of linters per ton, or approximately 10% of the weight of the seed. Practically all the fibers are removed from long staple cotton of the Sea Island type in the ginning operation, and the seed as received at the oil mill is essentially free of short fibers or linters. Varieties of bald cotton have recently been proposed as strictly oilseed crops. In these varieties, the bolls contain bald seed having neither long nor short cotton fibers attached. Up to the present time, these varieties have attained no commercial importance and their future is dependent not only on the development of strains producing a high yield of oil per acre and of machines for mechanically harvesting such a crop, but also on the future economic position of cotton.

The linters consist mainly of cellulose. The minor constituents are pectic substance, mineral constituents, nitrogenous constituents, waxes, resins, pigments, and water-soluble carbohydrates and other substances.

The second prominent subdivision of the cottonseed is the seed coat or hull. The hull comprises about 40% of the weight of the whole seed. However, in processing cottonseed for oil and meal, the yield of recovered hulls is only about 470 to 640 pounds per ton of seed crushed, since during the separation operation part of the hulls are left with the meats in order to adjust the protein content of the resultant meal. The hulls are frequently ground to produce a bran and most of the analyses reported in the literature for hulls have been made on this type of product. Cottonseed hull or

hull bran consists primarily of cellulose and hemicelluloses, pentosans, lignin, and tannins, as well as smaller quantities of protein, fat, and mineral constituents.

The remaining portion of the cottonseed is the kernel or meat which consists mainly of oil and protein. The latter products, as well as the pigments, have been treated in previous chapters, hence the present discussion will be limited to the carbohydrates, phosphorus-containing compounds, mineral constituents, nitrogenous constituents other than protein, vitamins, and various minor components which make up the kernels or meats. While some chemical investigations of these substances have been made on the kernels themselves, many of them have been made on cottonseed cake or meal. Since the latter products usually contain substantial amounts of hulls or hull bran, their presence must be borne in mind in interpreting any quantitative data reported for cake or meal. Where quantitative data are presented, it will be mentioned insofar as possible whether these were obtained on whole cottonseed, cottonseed kernels, or some product of cottonseed milling, such as cake or meal.

II. Cottonseed Linters

The chemical properties and physical characteristics of cotton linters have been investigated by Henderson[1] who reported that microscopic examination showed the linters to be identical in appearance to cotton fibers, differing only in length. The moisture content of air-dried linters was found to be 5.56% and of linters conditioned by contact with saturated air, 14.89%. The ash content was found to be 0.230%. When extracted with various solvents, the dried linters contained the following percentages of extractable material: water, 0.310; chloroform, 0.415; ethyl alcohol, 0.575. The composition of the extracts was not determined.

Although little work has been reported relative to the nature of the minor constituents of cottonseed linters, considerable information is available concerning the minor constituents of cotton fiber. Since the two products are so nearly alike, it may be assumed that the minor constituents of cotton fiber and the linters are relatively similar. While this assumption may not be strictly valid in a quantitative sense, it is probably justified from a qualitative viewpoint. Some variation in the composition of that portion of the fiber adhering to the seed coat after removal of the long fiber might be expected, but the same components as are present in the long fibers would probably be found on examination of the linters.

A. Cellulose

The structure of cellulose is shown in Figure 116. The cellulose molecule consists of a regular chain of β-glucose units joined in glucosidic

[1] W. F. Henderson, *Ind. Eng. Chem.*, **15**, 819–822 (1923).

union at the fourth carbon atom.[2] Its chain length has been estimated by various chemical and physical methods most of which indicate that the cellulose molecule comprises 100 to 200 β-glucose units. Cotton cellulose

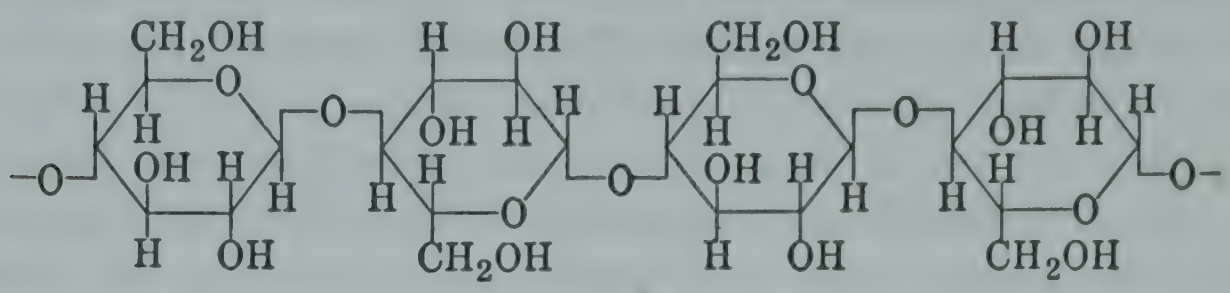


Fig. 116. Structure of the cellulose chain.

possesses a relatively invariable composition and is readily purified. For this reason it has been termed "normal cellulose" to distinguish it from other types of cellulose which are generally less homogenous and may contain units other than β-glucose in their chain.[3] The cellulose content of cotton linters generally varies from about 72 to 85%.

B. Pectic Substance

Pectic substances have been defined [4] as complex colloidal carbohydrate derivatives which occur in or are derived from plants and contain a large proportion of anhydrogalacturonic acid units which are thought to exist in chainlike combination. The term "pectic acids" is applied to pectic substances composed mainly of colloidal polygalacturonic acids and essentially free from methyl ester groups. The pectic substance of cotton fiber is not readily extracted by water except by boiling the cotton with water under pressure,[5] under which condition it is hydrolyzed to galacturonic acid. The pectic substance may be extracted from cotton fiber without alteration by a hot solution of 0.5% ammonium oxalate. The treatments required to extract the pectic substance from cotton fiber indicate that it is present in the fiber in the form of insoluble salts.[6, 7] Whistler, Martin, and Harris [7] concluded that a pectin–cellulose complex does not exist in cotton fibers. Viktorov and Fridlyand [8] found about 0.98% of pectic sub-

[2] E. F. Armstrong and K. F. Armstrong, *The Carbohydrates,* 5th ed., Longmans, Green, London, 1934, pp. 201–205.

[3] For further information on cellulose, the reader is referred to E. Ott, *Cellulose and Cellulose Derivatives,* Interscience, New York, 1943.

[4] American Chemical Society, "Report of the Committee for the Revision of the Nomenclature of Pectic Substances," *Chem. Eng. News,* **22,** 105–106 (1944).

[5] M. M. Chilikin and Z. S. Rozova, *J. Applied Chem. U.S.S.R.,* **10,** 709–715 (1937), summary in German, p. 716.

[6] S. A. Harris and H. J. Thompson, *Contrib. Boyce Thompson Inst.,* **9,** 1–5 (1937).

[7] R. L. Whistler, A. R. Martin, and M. Harris, *Textile Research,* **10,** 269–279 (1940); *Am. Dyestuff Rept.,* **29,** 244, 253–258 (1940); *J. Research Natl. Bur. Standards,* **24,** 555–565 (1940).

[8] P. P. Viktorov and G. I. Fridlyand, *J. Applied Chem. U.S.S.R.,* **12,** 113–123 (1939).

stance in the best American cotton. Less mature American cotton and Egyptian varieties of the same maturity had a somewhat higher content.

Harris and Thompson [6] isolated pectic acid equivalent to 0.68% of the weight of the cotton and compared its properties with those of pectic acid isolated from citrus fruit. This comparison is shown in Table 141.

TABLE 141

Comparison of Citrus and Cotton Pectic Acids[a]

Property	Purified pectic acid from citrus pectin	Purified pectic acid from ammonium oxalate extract of cotton
Specific rotation, $[\alpha]_D^{28}$	+240.5°[b]	+225.4°[c]
Neutralization equivalent	186	201
Carbon dioxide, %	19.9	21.8
Mucic acid, %	47.5	44.0

[a] S. A. Harris and H. J. Thompson, *Contrib. Boyce Thompson Inst.*, **9**, 1–5 (1937).
[b] Measured in 0.1 *N* NaOH, concentration = 0.919%.
[c] Measured in 0.1 *N* NaOH, co centration = 0.55%.

Chilikin and Rozova [5] investigated the products of hydrolysis of the pectic substance of cotton and found, in addition to galacturonic acid, a mixture of sugars containing arabinose, xylose, and fructose.

C. Mineral Constituents

Considerable variation in the ash content of raw cotton has been reported in the literature. The ash content of carefully cleaned cotton is usually about 1 to 1.5%. Values appreciably higher than 1.5% probably

TABLE 142

Mean Values of Ash Content and Ash Alkalinity of Different Types of Cotton[a]

Type and source	Number of samples analyzed	Ash, %	Ash alkalinity[b]	Ash alkalinity per gram ash[c]
North American	12	1.17	16.46	14.1
South American	7	1.16	16.67	14.3
Indian American	7	1.25	18.6	14.9
Other outside growths of American cotton	15	1.47	22.5	15.3
Egyptian	6	1.20	18.28	15.28
Egyptian	4	1.26	20.04	15.86
Native Indian	10	1.28	19.2	15.1
Sea Island	6	0.98	14.9	15.2

[a] R. G. Fargher and M. E. Probert, *J. Textile Inst.*, **17**, 46–52T (1926).
[b] Ash alkalinity is the number of milliequivalents of acid required to neutralize the ash from 100 g. of clean cotton.
[c] Ash alkalinity per gram ash is calculated by divid'ng the ash alkalinity by the percentage of ash.

arise from sand and dirt being associated with the sample taken for analysis. Birtwell, Clibbens, and Ridge [9] have standardized the method for determining the mineral constituents of cotton and have shown that it is sufficient for many purposes to measure the alkalinity of the ash, which is roughly proportional to the total ash in the cotton. They have defined ash alkalinity as the number of milliequivalents of acid needed to neutralize the ash from 100 g. of clean cotton. The mean values for the percentage of ash and the ash-alkalinity of various types of cotton as determined by Fargher and Probert [10] are shown in Table 142.

Geake [11] developed a rapid sedimetric method for the determination of the phosphorus content of cotton and applied the method to trade cottons of various origins. Sufficient variation was observed in the phosphorus content to differentiate cotton of American and Egyptian growth. The average phosphorus content of cotton from various sources is shown in Table 143.

TABLE 143

Average Phosphorus Content of Cotton from Different Sources[a]

Type and source	Phosphorus pentoxide, %	Type and source	Phosphorus pentoxide, %
American	0.05	Egyptian other than Sakellaridis	0.09
Sea Island	0.07	South American	0.07
Sakellaridis (Egyptian)	0.12		

[a] A. Geake, *J. Textile Inst.*, **15**, 81–93T (1924).

Walker and Quell [12] investigated the ash constituents and their probable distribution as salts in raw cotton. They found that ion exchange occurs when cotton is washed with aqueous salt solutions, the principal effect being the replacement of Mg^{++} by Ca^{++} in the case of calcium sulfate solutions, or the reverse in the case of magnesium sulfate solutions. The mineral constituents which they identified in seven analyses of raw cotton are shown in Table 144. The distribution of the various salts in the ash are shown in Table 145.

Walker and Quell also expressed the ash constituents as milliequivalents per 100 g. of dry cotton and determined by calculation that the ratio base/acid is 1.00. In calculating this ratio, magnesium, iron, and aluminum were neglected, since they were assumed to be present in the form of organic rather than inorganic salts.

[9] C. Birtwell, D. A. Clibbens, and B. P. Ridge, *J. Textile Inst.*, **14**, 297–313T (1923).
[10] R. G. Fargher and M. E. Probert, *J. Textile Inst.*, **17**, 46–52T (1926).
[11] A. Geake, *J. Textile Inst.*, **15**, 81–93T (1924).
[12] A. C. Walker and M. H. Quell, *J. Textile Inst.*, **24**, 131–144T (1933).

TABLE 144

Mineral Constituents of Cotton[a]

Constituent	Percentage of dry weight of cotton	Constituent	Percentage of dry weight of cotton
K	0.361	$Fe_2O_3 + Al_2O_3$	0.048
Na	0.030	P_2O_7	0.045
Ca	0.054	Cl	0.045
MgO	0.070		
CO_3	0.200	*Total*	1.046
SO_4	0.156		
SiO_3	0.037	Ash as weighed	1.049

[a] A. C. Walker and M. H. Quell, *J. Textile Inst.*, **24,** 131–144T (1933).

TABLE 145

Mineral Constituents of Cotton in the Form of Salts[a]

Salt	Percentage of dry weight of cotton	Salt	Percentage of dry weight of cotton
$CaSO_4$	0.054	$Fe_2O_3 + Al_2O_3$	0.048
$CaSiO_3$	0.029	NaCl	0.075
$CaCO_3$	0.070	$K_4P_2O_7$	0.087
K_2SO_4	0.214		
K_2SiO_3	0.036	*Total*	1.046
K_2CO_3	0.364		
MgO	0.069	Ash as weighed	1.049

[a] A. C. Walker and M. H. Quell, *J. Textile Inst.*, **24,** 131–144T (1933).

McHargue [13] reported the content of iron in cotton fiber to be 0.019%, compared to trace amounts of copper and manganese.

D. Nitrogenous Constituents

The nitrogenous constituents of raw cotton which occur only in small amounts are apparently proteinaceous in nature, although they have never been completely characterized. Ridge [14] developed a micro-Kjeldahl method for the accurate determination of the nitrogen content of raw cotton. He reported values of 0.180–0.399% for the nitrogen content of cotton from different sources.

Some of the coloring matter of cotton has been attributed to the presence of nitrogen-containing compounds. Bleaching agents containing hypochlorites destroy the color of cotton and simultaneously reduce its nitrogen content. However, the chemical changes which occur during the

[13] J. S. McHargue, *J. Am. Soc. Agron.*, **18,** 1076–1083 (1926).
[14] B. P. Ridge, *J. Textile Inst.*, **15,** 94–103T (1924).

bleaching process are unknown. Chilikin [15] reported the presence of a dark colored amino acid in the sodium hydroxide extract of cotton and claimed that hypochlorite converts the acid into a chloramine.

Haworth and MacDonald [16] isolated a small amount of histamine from cotton dust.

E. Wax and Resins

The presence of a coating of wax on cotton fibers was first reported by Schunck [17] in 1868. He separated a portion of wax from the fiber and found that it had a melting point of 83–84° C. and resembled carnauba wax. Since this melting point is higher than any subsequently reported value for the wax from the usual varieties of cotton, it may be assumed

TABLE 146

Properties of Wax from American and Egyptian Cottons[a]

Property	American cottons		Egyptian cotton
	Upland	Mississippi Delta	Sakellaridis
Melting point °C.	77	76.5	80
Density (15°C.)	0.985	0.976	0.990
Acid value	27	29	28
Saponification value	65	57	70
Acetyl value	64	84	83
Iodine value	19	27	20
Unsaponifiable matter, %	62	68	57
Acetyl value of unsaponifiable matter	133	124	115

[a] R. G. Fargher and L. Higginbotham, *J. Textile Inst.*, **15,** 419–433T (1924).

that the method used led to the isolation of one of the higher melting fractions. The literature reveals no further investigation of cotton wax until 1911 when Knecht and co-workers [18] began a series of investigations to determine its properties and components. Subsequently, Fargher and associates [19-21] developed methods for extracting the wax and separating

[15] M. M. Chilikin, *Bull. féd. intern. assoc. chim. text. couleur,* **1935,** No. 5, 367–385.
[16] E. Haworth and A. D. MacDonald, *J. Hyg.,* **37,** 234–242 (1937).
[17] E. Schunck, *Chem. News,* **17,** 118 (1868).
[18] E. Knecht and J. Allan, *J. Soc. Dyers Colourists,* **27,** 142–146 (1911). E. Knecht, *Textile Inst. J.,* **2,** 22–29 (1911). E. Knecht and W. Hall, *J. Soc. Dyers Colourists,* **34,** 220–225 (1918). E. Knecht and F. V. Fernandes, *ibid.,* **36,** 43–47 (1920). E. Knecht and G. H. Streat, *ibid.,* **39,** 73–77 (1923).
[19] R. G. Fargher and M. E. Probert, *J. Textile Inst.,* **14,** 49–65T (1923). R. G. Fargher, *Brit. Assoc. Advancement Sci. Rept.,* **1923,** 436. R. G. Fargher and L. Higginbotham, *J. Textile Inst.,* **15,** 75–80T (1924). P. H. Clifford, L. Higginbotham, and R. G. Fargher, *ibid.,* **15,** 120–137T (1924). P. H. Clifford and M. E. Probert, *ibid.,* **15,** 401–413T (1924). R. G. Fargher, *J. Soc. Dyers Colourists,* **40,** 283–285 (1924). L. V. Lecomber and M. E. Probert, *J. Textile Inst.,* **16,** 338–344T (1925). R. G. Fargher and L. Higginbotham, *ibid.,* **17,** 233–246T (1926). R. G. Fargher and L. Higginbotham, *ibid.,* **18,** 283–287T (1927).
[20] R. G. Fargher and M. E. Probert, *J. Textile Inst.,* **15,** 337–346T (1924).
[21] R. G. Fargher and L. Higginbotham, *J. Textile Inst.,* **15,** 419–433T (1924).

it into its various components. The properties of the wax extracted from American and Egyptian cottons by Fargher and Higginbotham [21] are shown in Table 146. By the use of various organic solvents, they were able

TABLE 147

Components of Cotton Wax; Fractions Extracted by Various Solvents[a,b]

Crude chloroform extract	*A* Light petroleum extract (85%)	*I* Sparingly soluble portion (31%)		Alcohols (23%)[c]: ceryl, montanyl, gossypyl, an alcohol $C_{32}H_{66}O$, and a glycol $C_{30}H_{62}O_2$ (?) Free acids (2%): montanic acid and an acid $C_{34}H_{68}O_2$[c] Combined acids[c]: carnaubic, montanic, and melissic acids
		II Readily soluble (54%), divided by means of alcohol into	*II–a* Soluble in cold alcohol (40%)	Alcohols (10%): glycerol, a phytosterol, $C_{29}H_{50}O$, amyrin, and amorphous resinols Free acids (17%): palmitic, stearic, oleic, carnaubic, isobehenic, and amorphous resin acids Combined acids (6%): palmitic, stearic, oleic, acid $C_{20}H_{38}O_2$, and lignoceric acid Unsaturated liquid hydrocarbons
			II–b Insoluble in cold alcohol (12%)	Gossypyl carnaubate Montanic acid, free and combined C_{28} and C_{30} alcohols Triacontane
			II–c Insoluble in boiling alcohol (2%)	Amorphous resin esters
	B Ether extract (8%)			Phytosterolin, $C_{35}H_{60}O_6$ (6%); gossypyl gossypate (2%)
	C Benzene extract (2%)			Wax esters, principally montanyl montanate
	D Chloroform extract (1%)			Phytosterolin, $C_{35}H_{60}O_6$

[a] R. G. Fargher and L. Higginbotham, *J. Textile Inst.*, **15**, 419–433T (1924).

[b] This table represents the fractionation of the components of the wax from Egyptian cotton. Similar results were obtained with the wax from American cotton except that the latter contained a smaller proportion of wax esters and contained sitosterol and sitosterol glucoside in place of the phytosterol, $C_{29}H_{50}O$, and its glucoside.

[c] It has since been recommended by A. C. Chibnall, S. H. Piper, A. Pollard, E. F. Williams, and P. N. Sahai, *Biochem. J.*, **28**, 2189–2208 (1934), that the names ceryl alcohol, montanyl alcohol, gossypyl alcohol, carnaubic acid, montanic acid, and melissic acid be abandoned, since the substances given these names have been shown to be mixtures of two or more alcohols or acids.

to separate the wax into fractions of different compositions. The procedure of fractionation and the components of the fractions are indicated in Table 147. The principal components were stated to be long-chain alcohols and acids, saturated and unsaturated hydrocarbons, resins and resin acids, sterols, and sterol glucosides.

Since these investigations were completed, much more precise methods for the elucidation of wax structure have been developed by Chibnall and associates. Their methods are based on precise measurement of various physical properties of the fatty acids, fatty alcohols, and saturated hydrocarbons isolated from a wax and a comparison of these properties with those of the corresponding pure synthetic compounds or mixtures thereof. Utilizing these methods, Chibnall, Piper, Pollard, Williams, and Sahai [22] investigated the composition of the wax of American cotton which had been previously examined by Fargher and Probert.[20] They found that the alcohols designated as "montanyl" alcohol ($C_{28}H_{58}O$), "gossypyl" alcohol ($C_{30}H_{62}O$), and the C_{32} and C_{34} alcohols were in reality mixtures of two or more alcohols. The probable constitution of the primary alcohols of American cotton wax as determined by Chibnall *et al.* is shown in Table 148. All of the even-numbered primary alcohols from C_{28} to C_{34} were found to be present in the wax but the isolated products were not pure alcohols but instead were mixtures. Similarily, the acids which had

TABLE 148

Probable Constitution of the Primary Alcohols of American Cotton Wax[a]

Alcohols and mixtures	Alcohol, m.p., °C.	Acetate, m.p., °C.	Derived acid, m.p., °C.
Montanyl alcohol (C_{28})[b,c]	83.5	67–67.5	83.5–84
Suggested mixture: 40% C_{28} + 40% C_{30} + 20% C_{32}	83.8	68	86.6
Gossypyl alcohol (C_{30})[b,c]	85.0	69–69.5	86.5
Suggested mixture: 20% C_{28} + 40% C_{30} + 40% C_{32}	85.4	69.5	87.9
Alcohol (C_{32})[b]	87–87.5	72.5	88–89
Suggested mixture: equimolar C_{30} + C_{32} + C_{34}	87.1	72.7	90
Alcohol (C_{34})[b]	88.5–89	74.5	90–91
Suggested mixture: 50% C_{32} + 50% C_{34}	89.4	74.5	93.1
Suggested mixture: 20% C_{30} + 40% C_{32} + 40% C_{34}	88.2	73.2	91.1

[a] A. C. Chibnall, S. H. Piper, A. Pollard, E. F. Williams, and P. N. Sahai, *Biochem. J.*, **28**, 2189–2208 (1934).

[b] From data of R. G. Fargher and M. E. Probert, *J. Textile Inst.*, **15**, 337–346T (1924).

[c] Chibnall *et al.* have recommended that the names montanyl alcohol and gossypyl alcohol be abandoned, since the substances so designated have been shown to be mixtures of two or more alcohols.

[22] A. C. Chibnall, S. H. Piper, A. Pollard, E. F. Williams, and P. N. Sahai, *Biochem. J.*, **28**, 2189–2208 (1934).

been isolated previously were shown to be mixtures of the even-numbered normal fatty acids from C_{24} to C_{34} and the possible presence of shorter chain acids was indicated. Fargher and Probert had previously reported the isolation of two paraffins which they considered to contain C_{30} and C_{31} skeletons. Power and Chestnut [23] isolated a paraffin melting at 62° C. which they considered to be triacontane, $C_{30}H_{62}$. Chibnall and co-workers [22] examined the latter product and found it to comprise a mixture of four or more paraffins. As a result of their investigation of these and other waxes, Chibnall *et al.* concluded that "all the names which have been assigned by previous workers to primary alcohols, fatty acids, and paraffins isolated from waxes have been given to products that are not chemical entities but mixtures." They therefore recommended that the names which had been given to these products that are mixtures be abandoned. Among the names which had been applied to products from cotton wax and recommended for abandonment are the following: ceryl alcohol, montanyl alcohol, gossypyl alcohol, carnaubic acid, montanic acid, and mellisic acid.

The amount of wax which may be extracted from cotton lint with organic solvents normally ranges from 0.4 to 0.7%. However, Conrad [24] found that green lint cotton, *Gossypium hirsutum* (var. Arkansas green lint) contained a much higher percentage of wax, namely, 14 to 17%. This wax was also found to have a somewhat higher melting point than that from other varieties of cotton. Fractions obtained by separation with 95% alcohol and ethyl ether had melting ranges of 85–89°, 86.5–90°, and 93–95° C. Tonn and Schoch [24a] have recently reported some of the properties of cotton wax extracted from Texas cotton fiber and have determined the solubility–temperature curves for this wax in a number of common organic solvents.

F. Coloring Matter

There is considerable difference of opinion and a lack of chemical evidence as to the true nature of the constituents responsible for the color of cotton fiber. Henderson [25] obtained a slightly yellow-colored solution by leaching cotton linters with strong hydrochloric acid. The extract gave a test for ferric ion when treated with ammonium thiocyanate. He concluded that the color extracted from linters was due to the presence of iron salts. However, this is probably an oversimplification of the pigment problem, since the iron is probably combined with organic acids in a complex manner. Also, it does not account for the coloring matter in cotton which may be red, yellow, or green.

[23] F. B. Power and V. K. Chestnut, *J. Am. Chem. Soc.*, **47**, 1751–1774 (1925).
[24] C. M. Conrad, *Science*, **94**, 113 (1941).
[24a] W. H. Tonn, Jr., and E. P. Schoch, *Ind. Eng. Chem.*, **38**, 413–416 (1946).
[25] W. F. Henderson, *Ind. Eng. Chem.*, **15**, 819–822 (1923).

G. Water-Soluble Constituents

McCall and Guthrie[26] recently determined the organic acid content of raw cotton fiber. In 4 samples of cotton they found 0.32 to 0.57% of malic acid, 0.05 to 0.10% of citric acid, and 0.002 to 0.005% of oxalic acid. The quantities of unidentified and total organic acids were calculated to be 0.24 to 0.40% and 0.77 to 0.91%, respectively. By extracting the cotton with boiling water, they were able to isolate and subsequently identify *l*-malic acid and citric acid in the aqueous extract.

Compton and Haver[27] have determined the nature of the reducing sugars extracted by means of cold water from cotton fibers of different degrees of maturity. The total amount of reducing sugars in the cotton fiber was found to decrease as the plant matured until a value of about 0.3 to 0.8% was reached from 40 to 50 days after flowering. Fifty days after flowering the amount of glucose, fructose, and pentose in the fiber, calculated as percentage of total sugars, was found to be 10.1, 77.4, and 12.5, respectively.

Sherwood and Singer[28] reported the presence of 0.028 μg. per g. of folic acid in cotton fiber, and Robbins and Ma[29] found evidence of the presence of biotin, thiamin, and pyridoxine in cotton batting.

III. Cottonseed Hulls

A rather complete analysis of cottonseed hull bran was reported by Markley[30] for a bran from which the fibers had been removed by air separation. The proximate analysis on an air-dry and on an oven-dry basis

TABLE 149

Proximate Analysis of Cottonseed Hull Bran[a]

Constituent	Air-dry, %	Oven-dry, %	Constituent	Air-dry, %	Oven-dry, %
Moisture	12.25	—	Crude protein	2.88	3.28
Ash	2.09	2.38	Crude fiber	32.48	37.01
Crude fat	0.80	0.91	Nitrogen-free extract	49.50	56.42

[a] K. S. Markley, *J. Am. Soc. Agron.*, **20,** 1102–1107 (1928).

is shown in Table 149. The content of the nonnitrogenous constituents of cottonseed hull bran is shown in Table 150 and the composition of the Cross and Bevan cellulose is given in Table 151. The author concluded

[26] E. R. McCall and J. D. Guthrie, *J. Am. Chem. Soc.*, **67,** 2220–2221 (1945).
[27] J. Compton and F. E. Haver, Jr., *Contrib. Boyce Thompson Inst.*, **11,** 281–290 (1940).
[28] M. B. Sherwood and E. D. Singer, *J. Biol. Chem.*, **155,** 361–362 (1944).
[29] W. J. Robbins and R. Ma, *Bull. Torrey Botan. Club*, **69,** 184–203 (1942).
[30] K. S. Markley, *J. Am. Soc. Agron.*, **20,** 1102–1107 (1928).

TABLE 150

Nonnitrogenous Constituents of Cottonseed Hull Bran[a]

Component	Air-dry, %	Oven-dry, %
Furfural, yield by distillation	22.23	25.33
Furfural, expressed as pentose	43.21	49.24
Furfural, expressed as pentosan	38.02	43.33
Dextrose, 50% alcoholic extract	Trace	—
Sucrose, 50% alcoholic extract	None	—
Galactose	Present	—
Reducing sugar after hydrolysis, calculated as dextrose	37.59	42.84
Reducing sugar after hydrolysis, calculated as xylose	38.24	43.58
Crude cellulose	45.36	51.7
Lignin	20.91	23.83

[a] K. S. Markley, *J. Am. Soc. Agron.*, **20,** 1102–1107 (1928).

TABLE 151

Composition of Cross and Bevan Cellulose[a]

Constituent	Crude cellulose, %	Cottonseed hull bran	
		Air-dry, %	Oven-dry, %
Crude cellulose	—	45.55	51.91
Ash	0.42	0.19	0.22
Pentosan	36.17	16.48	18.78
Alpha cellulose[b]	45.65	20.79	23.70
Beta cellulose	15.3	6.97	7.94

[a] K. S. Markley, *J. Am. Soc. Agron.*, **20,** 1102–1107 (1928).
[b] Uncorrected for pentosan and ash; corrected value is 43.97%.

TABLE 152

Composition of Oven-Dried Cottonseed Hull Bran[a]

Component	Per cent by weight	Component	Per cent by weight
Cross and Bevan cellulose	53.40	Methoxyl	2.16
Pentosans in Cross and Bevan cellulose	19.05	Acetic acid by hydrolysis	4.98
Hydrolysis number (loss in cellulose due to 15% H_2SO_4 hydrolysis)	33.40	Ash	2.28
		Ether-soluble	0.27
Furfural, yield by distillation	22.50	1% alkali-soluble	20.22
Total pentosans	38.40	Cold water-soluble	1.87
Lignin	23.40	Hot water-soluble	7.52
Nitrogen (Kjeldahl) in lignin	0.52		
Total nitrogen (Kjeldahl)	0.54		

[a] D. M. Musser, *J. Assoc. Official Agr. Chem.*, **22,** 420–422 (1939). Original hull bran contained 8.11% moisture

that the cottonseed hull had a greater potential commercial value than had been previously recognized.

Musser[31] has since reported an analysis of cottonseed hull bran, and his results are in close agreement with those of Markley insofar as they are comparable. The composition of the cottonseed hull bran as reported by Musser is shown in Table 152.

As may be seen from Tables 149–152, dry cottonseed hulls contain about 50% crude celluloses or cellulose complexes which contain pentosans as well as alpha and beta cellulose. In addition, the hulls yield about 23 to 25% each of lignin and furfural.

Schreiber *et al.*[32] have reported the isolation of xylose from cottonseed hulls and claim a yield of 26% of this pentose in crystalline form.

A. Hemicelluloses

The characteristics and composition of the hemicelluloses present in cottonseed hulls have been determined by Anderson and co-workers.[33] They found the hemicelluloses of cottonseed hulls to be polyuronides of D-glucuronic acid and D-xylose in which 1 mole of the acid is combined

TABLE 153

Analysis of Hemicelluloses from Cottonseed Hulls after Treatment with Bromine Water[a]

Hemicellulose fraction	Xylan, %	Uronic acid, %	Total, %	$[\alpha]_D^{25}$, degrees	Xylose per mole uronic acid, moles
A	92.20	8.50	100.70	−95.86	15.9
A_1	92.23	8.60	100.83	−91.49	15.6
A_2	90.70	10.00	100.70	−91.10	13.2
B	87.24	11.77	99.01	−80.48	11.0
B_1	90.31	12.39	102.70	−81.64	10.1
B_2	91.15	11.68	102.83	−77.26	11.0

[a] E. Anderson, J. Hechtman, and M. Seeley, *J. Biol. Chem.*, **126,** 175–179 (1938).

with from approximately 10 to 16 moles of the sugar. From the products of hydrolysis, an aldobionic acid in the form of its barium salt was isolated.

The hemicelluloses were extracted with a cold 5% solution of sodium hydroxide from cottonseed hull bran which had first been thoroughly extracted with boiling acetone, ethanol, and water. After two alkaline

[31] D. M. Musser, *J. Assoc. Official Agr. Chem.*, **22,** 420–422 (1939).

[32] W. T. Schreiber, N. V. Geib, B. Wingfield, and S. F. Acree, *Ind. Eng. Chem.*, **22,** 497–501 (1930).

[33] E. Anderson, *J. Biol. Chem.*, **91,** 559–568 (1931). E. Anderson, and S. Kinsman, *ibid.*, **94,** 39–47 (1931). E. Anderson, J. Hechtman, and M. Seeley, *ibid.*, **126,** 175–179 (1938).

extractions of 48 hours each, the combined filtrates were made slightly acid with hydrochloric acid and the water-insoluble hemicellulose *A* was centrifuged out. Water-soluble hemicellulose *B* was precipitated from the centrifugate by the addition of ethanol. Both products are mixtures whose composition depends on the exact procedure followed in their isolation. The hemicelluloses when separated from cottonseed hulls also contained a substance *X* which imparted color to the isolated product. It was found that this *X*-body could be removed by chlorination or bromination of the isolated hemicellulose, so that a perfectly white product could be prepared. The analysis of hemicelluloses isolated from cottonseed hulls and purified by treatment with bromine water is shown in Table 153.

A and *B* are the initial water-insoluble and water-soluble fractions. By dissolving fractions *A* and *B* in sodium hydroxide and acidifying the solution, they were further separated into insoluble fractions A_1 and B_1 and soluble fractions A_2 and B_2. Hemicellulose fractions A_1 and B_2 were obtained in relatively large amounts, whereas the yield of hemicellulose fractions A_2 and B_1 were small.

B. Mineral Constituents

The most complete analysis of cottonseed hulls for mineral constituents has been made by McHargue,[13] who determined the percentage of various elements present in hulls separated by hand from a sample of cottonseed grown in Mississippi. The results of this analysis are shown in Table 154.

TABLE 154

Mineral Constituents of Cottonseed Hulls and Their Crude Ash (Moisture-Free Basis)[a]

Constituent	In hulls, %[b]	In crude ash, %	Constituent	In hulls, %[b]	In crude ash, %
Ash (crude)	2.679	—	Calcium	0.1355	5.06
Copper	0.0014	0.0512	Magnesium	0.1283	4.79
Iron	0.0246	0.917	Phosphorus	0.1339	5.00
Manganese	0.0137	0.512	Potassium	1.132	42.26
Zinc	0.0022	0.082	Sodium	0.870	32.46

[a] J. S. McHargue, *J. Am. Soc. Agron.*, **18**, 1076–1083 (1926).

[b] Owing to some apparent discrepancies in the values reported in the original table, these data have been recalculated by the authors from the percentages of the various constituents reported in the crude ash and the percentage of crude ash in the hulls.

McHargue attributes the relatively high-manganese content of the hulls, compared to other parts of the cotton plant, to the fact that the testa or seed coat, which usually has a high-manganese content, remains firmly attached to the inside of the hull on dissection.

Musser [31] made a qualitative spectrographic analysis of ashed hulls.

The analysis indicated the presence of large quantities of calcium, magnesium, sodium, and potassium—smaller quantities of iron, manganese, copper, boron, phosphorus, silicon, barium, and aluminum—and traces of zinc and nickel. Dahle [34] reported the presence of 12 to 14 p.p.m. of fluorine in cottonseed hulls.

C. Lignin

Markley [30] found the lignin content of a sample of cottonseed hull bran to be 20.91% on an air-dry basis or 23.83% on an oven-dry basis. Attempts to isolate pure lignin by extraction with cold 2% alcoholic sodium hydroxide gave, besides lignin, a dark red pigment. This pigment did not give the characteristic test for tannins and phlobaphenes, and was thought to be primarily a xylan body.

Odintzov, Tsuipkina, and Ergorova [35] found that the lignin of cottonseed hulls that had been treated with alkali could be separated into two fractions, one of which was soluble in alcohol and the other insoluble in alcohol but soluble in water. The ratio of the soluble to the insoluble fraction was found to be about 1 : 2. They believe that the resin or substance *X* mentioned in the literature is an intermediate product between tannin and lignin.

D. Tannins

Cottonseed hulls contain some tannins. Zakoshchikov and co-workers [36] have reported that young plants yield hulls containing as high as 12% tannins. However, hulls from ripe plants contained only 7% tannins. They extracted the tannins from the hulls with hot water and tested their tanning properties. By contrast, Odintzov, Tsuipkina, and Ergorova [35] reported that they found very little true tannin in cottonseed hulls and claimed that the hulls were unsuited for use in tanning. Some of the differences reported by various workers for the lignin and tannin content of cottonseed hulls result from the methods of analysis used, most of which do not permit a clear distinction to be drawn between these and related substances which may be present in products of this type.

IV. Cottonseed Meats and Meal

A. Carbohydrates

Oil and protein, which have been discussed in previous chapters, make up and bulk of the cottonseed kernel or meat. From the standpoint of quantity, the next most important component or group of components of

[34] D. Dahle, *J. Assoc. Official Agr. Chem.*, **21**, 594–595 (1938).

[35] P. N. Odintzov, M. N. Tsuipkina, and L. V. Ergorova, *J. Applied Chem. U.S.S.R.*, **9**, 119–138 (1936), summary in French, p. 139.

[36] A. P. Zakoshchikov, V. T. Ivanova, G. A. Korzheniovskii, and A. M. Kurennova, *Trest Khlopkoochistitel. Prom. U.S.S.R.* (Cotton Ind. Trust), **No. 1**, 102–115 (1933).

the cottonseed kernel are the carbohydrates. The carbohydrate fraction of cottonseed meal has never been thoroughly investigated. Mirer [37] analyzed the kernels from two grades of Transcaucasian cottonseeds. The total carbohydrate contents calculated on the weight of the dry kernels was reported to be 13.5 and 14.08%, respectively; crystalline sugars—including monosaccharides, hydrolyzed raffinose (fructose, ½ melibiose), sucrose, and related sugars—7.29 and 7.9%; colloidal sugars (dextrins, soluble pectins, etc.), 0.41 and 0.65%; hemicellulose and pectin-like substances, 3.3 and 3.36%; and cellulose, 2.15 and 2.17%. No starch was found in these kernels. Although this analysis appears rather complete with respect to the general classes and amounts of the various carbohydrates present in the cottonseed kernel, it does not provide quantitative information on the specific carbohydrates which are present.

1. Starch

In a microchemical investigation of the cottonseed, Reeves and Valle [38] found the amount of the starch in mature seed to be very small; they found also that the starch grains themselves were very small and did not possess the lamellae, characteristic of those present in many other plants. In many seeds, it was extremely difficult to find starch grains, but occasionally a seed was observed to contain large masses of them. In any case, the starch grains were observed only after staining with iodine. The small amount of starch present and the difficulty of observing the starch grains probably account for the numerous reports that starch is absent in mature cottonseed meats.

2. Pentosans and Pentoses

According to Malowan,[39] as well as other investigators, the quantity of pentosans in hulled cottonseed is usually about 5 or 6%. Reeves and Valle [38] concluded, on the basis of microchemical tests, that the only part of the cottonseed embryo which gave any reaction for pentosans was the resin gland. The test was made by a modification of the phloroglucinol reaction,[40] in which a red color is formed when pentosans and phloroglucinol are allowed to react for 20 minutes without heating. In the microchemical test, heat was usually required to develop the red color. Gurevich [41] found that resin glands and pure gossypol gave, with orcinol and phloroglucinol in hydrochloric acid at room temperature, an identical

[37] E. A. Mirer, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1936,** 49–54, summary in English, p. 54.

[38] R. G. Reeves and C. C. Valle, *Botan. Gaz.,* **93,** 259–277 (1932).

[39] J. Malowan, *Cotton Oil Press,* **5,** 40–43 (1921).

[40] *Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists,* 5th. ed., Assoc. Official Agr. Chem., Washington, 1940, pp. 361–362.

[41] M. Gurevich, *Masloboino Zhirovoe Delo,* **11,** 301–302 (1935); *Vsesoyuz, Nauch. Issledovatel. Inst. Zhirov,* **1936,** 31–41, summary in English, pp. 41–42.

red reaction. Xylose gave a red color with phloroglucinol and a green color with orcinol only on heating. He concluded that the observation of Reeves and Valle was probably due to the presence of gossypol in the resin glands rather than to pentosans. However, on boiling specimens previously freed from gossypol with orcinol and phloroglucinol in hydrochloric acid, the presence of pentosans in the cellular integuments of the ovule was established.

The fact that the carbohydrates of the cottonseed may not always occur as separate entities but may be present in the form of complexes is indicated by the work of Jones and Csonka [42] on proteins of the cottonseed. They isolated, from solvent-extracted cottonseed kernels, 2.08% of a pentose protein, by concentrating the filtrate from the dialyzed globulins *in vacuo* and precipitating the complex with ethanol. This complex contained 16.57% pentose, 0.194% phosphorus, and 12.64% nitrogen.

In their investigation of the allergens of cottonseed, Spies, Bernton, and Stevens [43] isolated an allergenic fraction, designated as CS-1, which was composed primarily of a protein and a polysaccharide. On acid hydrolysis, a pentose was formed from this complex. The allergenic properties of this fraction were attributed to the protein component.

3. Raffinose

The principal component of the carbohydrate fraction of the cottonseed kernel is raffinose. Because this is the only carbohydrate component which has been extensively investigated, and since cottonseed meal is considered to be one of the best sources for the preparation of this sugar, it will be discussed in some detail.

Raffinose, which is the best known trisaccharide, occurs to the extent of 4 to 9% or more in cottonseed meal. Its melting point is 118–119° C. and its specific rotation, $[\alpha]_D$, is $+104°$ (hydrate). Its constitutional formula may be represented as follows: [44]

$$\underset{\text{fructose}}{C_6H_{11}O_5}\text{—O—}\underset{\text{glucose}}{C_6H_{10}O_4}\text{—O—}\underset{\text{galactose}}{C_6H_{11}O_5}$$

(sucrose) (melibiose)

Raffinose itself has no reducing power, but it is converted completely by strong mineral acids to the monosaccharides, fructose, glucose, and galactose. More dilute acids effect only partial hydrolysis, *i.e.*, to produce fructose and melibiose. By choosing the proper enzyme system, either one or both of the glycoside linkages can be selectively hydrolyzed.

[42] D. B. Jones and F. A. Csonka, *J. Biol. Chem.*, **64,** 673–683 (1925).

[43] J. R. Spies, H. S. Bernton, and H. Stevens, *J. Allergy,* **10,** 113–129 (1939); *J. Am. Chem. Soc.,* **63,** 2163–2169 (1941).

[44] For proof of structure, see E. F. Armstrong and K. F. Armstrong, *The Carbohydrates,* 5th. ed., Longmans, Green, London, 1934, p. 184; or W. Charlton, W. N. Haworth, and W. J. Hickinbottom, *J. Chem. Soc.,* **1927,** 1527–1536.

About 1884, two German chemists working independently reported the isolation of a crystalline sugar from cottonseed press cake. Boehm [45] designated the sugar which he isolated "gossypose." Ritthausen [46] found the sugar which he isolated to have the same properties as the sugar which Berthelot had previously isolated from the manna of the eucalyptus tree and had called "melitose." The sugars from cottonseed press cake and manna were found by Ritthausen [47] to be identical. However, he acknowledged Boehm's priority to the discovery, since the latter had actually disclosed it in 1883 although it was not recorded in the literature until the following year. Scheibler [48] compared the properties of the sugar, which Boehm and Ritthausen had isolated from cottonseed cake, with raffinose, which had been isolated from sugar beets by Loiseau—and found them to be identical.

Since the original work on the isolation of raffinose from cottonseed cake, a number of investigators have proposed improved methods of preparations. Zitkowski [49] published a method in 1910 in which cottonseed meal was extracted with water and raffinose was precipitated from the extract as the calcium compound. A purity of 97.5% was claimed for this process but the yield was only about 1%, based on the weight of the meal used. Hudson and Harding [50] also proposed a method for the preparation of raffinose which gave yields on a laboratory scale of 2.5 to 4%. Clark [51] extracted cottonseed meal by percolation with water and obtained yields comparable with those of Hudson and Harding on purification of the raffinose. In 1923, Harding [52] reviewed the history of raffinose and its methods of preparation. He suggested a method for preparing this sugar in which the meal is treated with aluminum sulfate to suppress the extraction of undesirable constituents, thereby simplifying the subsequent purification. According to Harding, an average yield of 2.25% is all that can be reasonably expected in the preparation of a pure raffinose from cottonseed meal, and this, only if the preparation is carried out rapidly and the procedure closely followed. Englis and co-workers [53] used methanol as the extraction medium and obtained a yield of 2.5% raffinose. Bridel and Desmaret [54] described a percolation method of extraction using 60%

[45] Boehm, *Ges. z. Beförd d. gesamt. Nat.-Wissensch. z. Marburg* (June 13, 1883); *Arch. Pharm.*, **22,** 159 (1884).
[46] H. Ritthausen, *J. prakt. Chem.*, **29,** 351–357 (1884).
[47] H. Ritthausen, *J. prakt. Chem.*, **30,** 37 (1884).
[48] C. Scheibler, *Ber.*, **18,** 1779–1786 (1885).
[49] H. E. Zitkowski, *Am. Sugar Ind.*, **12,** 324–325 (1910).
[50] C. S. Hudson and T. S. Harding, *J. Am. Chem. Soc.*, **36,** 2110–2114 (1914).
[51] E. P. Clark, *J. Am. Chem Soc.*, **44,** 210–213 (1922).
[52] T. S. Harding, *Sugar*, **25,** 308–310 (1923).
[53] D. T. Englis, R. T. Decker, and A. B. Adams, *J. Am. Chem. Soc.*, **47,** 2724–2726 (1925).
[54] M. Bridel and M. Desmaret, *J. pharm. chim.*, **7,** 433–447 (1928); *Bull. soc. chim. biol.*, **10,** 510–521 (1928).

ethanol as the solvent, by means of which they obtained a yield of 3.3% raffinose.

Raffinose has never assumed any commercial importance and, although cottonseed meal is the best source of this sugar, containing as is reported from 4 to over 9%,[50] its isolation has been accomplished only in much lower yields; therefore, its production would not be very economical. If properties of cottonseed protein should be found which render them suitable for industrial utilization on an economic basis, the liquors formed as a by-product of the protein isolation would contain this sugar or the products of its hydrolysis. This "sweet-water" might serve as a suitable source of raffinose, or perhaps more profitably, as a medium for the growth of yeast for food or feed purposes. The feasibility of a process for yeast production from such waste liquors has been demonstrated on a laboratory scale in the case of the by-product liquor from the isolation of peanut protein.[55, 56]

B. Phosphorus-Containing Compounds

The phosphorus content of the cottonseed kernel has been determined by McHargue,[13] who found 1.79% of this constituent in a cottonseed grown in Mississippi. This value is somewhat higher than that reported by Lishkevich [57] for the kernels from 6 grades of cottonseed from Central Asia and the Caucasus, which ranged from 0.80 to 1.0%. Fontaine, Pons, and Irving [58] recently reported 1.53% total phosphorus in cottonseed meal which had been extracted with ethyl ether. The variations which have been noted are probably due to the variation in the soil types or fertilizer application during the growth of the cotton.

Lishkevich [57] found about 75% of the phosphorus in the cottonseed kernel to be present as phytin, 5 to 6% as phosphatides, and the balance as phosphoproteins and an insoluble fraction. Of the total phosphorus in ether-extracted cottonseed meal, Fontaine *et al.*[58] found 5.21% to be present as inorganic phosphorus. The remainder was assumed to be present in the form of organic compounds, mainly phytic acid or phytin, with smaller amounts of phosphatides and perhaps phosphoproteins.

1. Phytic Acid and Phytin

In cottonseed, as in most other oilseeds, the phosphorus occurs principally in the form of phytic acid or phytin. Phytic acid is inositol hexaphosphoric acid (see formula represented on page 485). Phytin is the calcium,

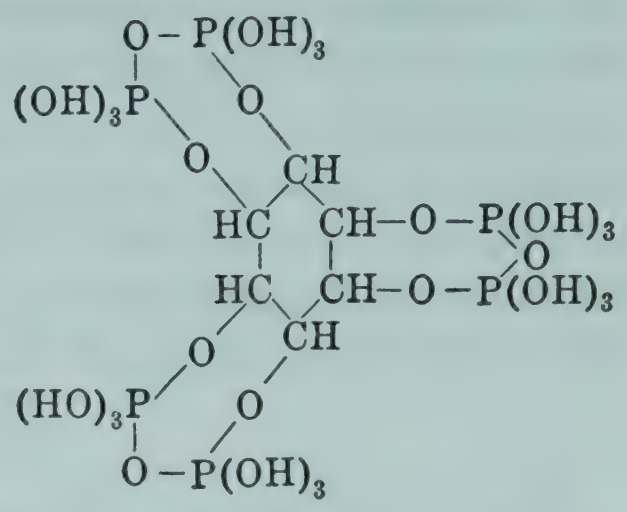
[55] T. J. Klatt, E. D. Parker, A. F. Pomes, and N. Porges, *Oil & Soap,* **22,** 319–321 (1945).

[56] R. S. Burnett, *Chem. Eng. News.,* **24,** 478–480 (1946).

[57] M. I. Lishkevich, *Masloboino Zhirovoe Delo,* **13,** No. 4, 20–22 (1937); **13,** No. 6, 9–10 (1937).

[58] T. D. Fontaine, W. A. Pons, Jr., and G. W. Irving, Jr., *J. Biol. Chem.,* **164,** 487–507 (1946).

magnesium, and potassium salt of phytic acid. Its composition is somewhat variable and is dependent upon the amount and relative proportions of the mineral constituents present in the seed, and hence available for formation of phytin from phytic acid.



phytic acid

In 1892, Hardin [59] examined aqueous solutions of cottonseed meal and concluded that they contained both meta- and pyrophosphoric acids. His evidence was based on the fact that the phosphorus in these solutions would diffuse through a semipermeable membrane, and on treatment with certain reagents gave precipitation reactions characteristic of the phosphoric acids. Crawford,[60] in 1910, observed a toxicity in certain cottonseed meals fed to rabbits and attributed it to salts of pyrophosphoric acid which he claimed had been formed during heat-treatment of the meal. He made the observation that the phosphorus appeared in some of the meals as a simple salt of phosphoric acid, while in others it appeared in a more complex organic form.

The true nature of the organic phosphoric acid compounds in cottonseed was elucidated in a series of papers by Rather [61] and by Anderson.[62] Although Anderson obtained the hexaphosphate of inositol, Rather obtained only the pentaphosphoric acid derivative. This apparent discrepancy is readily explicable on the basis of the activity of the enzyme, phytase,[63] which has been found in many seeds and is known to liberate phosphoric acid and inositol by hydrolysis of phytic acid or phytin. The particular phosphoric acid derivative of inositol which can be isolated from a given sample of cottonseed or cottonseed meal is thus determined by the history of the sample and the conditions of extraction. In the dormant seed, the organic phosphoric acid is probably present almost entirely as phytin or phytic acid. However, if the moisture content is increased, the activity of the phytase will be increased and the nature of the phosphoric acid compounds of inositol will be changed.

Fontaine, Pons, and Irving [58] investigated the protein–phytic acid relationship in ether-extracted cottonseed meal. Figure 108 (page 452) illustrates the solubility of the nitrogen and phosphorus compounds in

[59] M. B. Hardin, *South Carolina Agr. Expt. Sta. Bull.*, **8,** New Series (1892).
[60] A. C. Crawford, *J. Pharmacol.*, **1,** 519–548 (1910).
[61] J. B. Rather, *Texas Agr. Expt. Sta. Bull.*, **146,** 3–16 (1912); *J. Am. Chem. Soc.*, **35,** 890–895 (1913); **39,** 777–789 (1917); **39,** 2506–2515 (1917); *Arkansas Agr. Expt. Sta. Bull.*, **138,** 3–16 (1917); *J. Am. Chem. Soc.*, **40,** 523–536 (1918).
[62] R. J. Anderson, *New York Agr. Expt. Sta. Tech. Bull.*, **25,** 3–12 (1912); *J. Biol. Chem.*, **13,** 311–323 (1913); **17,** 141–150 (1914).
[63] H. P. Averill and C. G. King, *J. Am. Chem. Soc.*, **48,** 724–728 (1926).

cottonseed meal extracts, as a function of *p*H. A minimum total phosphorus solubility (17%) was observed at a *p*H of approximately 2.75. The maximum phosphorus solubility (85%) occurred at *p*H 0.70 and 6.0. Results of the analysis of cottonseed meal extracts for inorganic phosphorus is also shown in this figure. The maximum solubility of inorganic phosphorus indicates that the optimum range for cottonseed phytase activity lies between *p*H 4.0 and 5.0 at 25° C. A method has been proposed for the preparation of phytic acid from cottonseed meals by extraction with dilute acid at *p*H 5.75.

2. Phosphatides

The phosphatides of cottonseed, as well as of other oilseeds, are found in both the oil and meal. The amount of phosphatides which is extracted with the oil depends on the method of pressing or extraction and on the pretreatment of the seed, particularly on the adjustment of its moisture content.

Lishkevich [64] separated the phosphatides from cottonseed into three fractions: acetone-soluble (16.5%), alcohol-soluble (76.5%), and benzene-soluble (7.0%). The acetone-soluble fraction contained 46.2% lecithin and 53.8% cephalin. The alcohol-soluble fraction contained 53.2 to 59.4% lecithin and 40.6 to 46.8% cephalin. The benzene-soluble fraction was practically all lecithin.

Since the phosphatides are closely related to the oil, they have been discussed more fully in Chapter VII, Cottonseed Oil (see pages 377–379).

C. Mineral Constituents

The mineral constituents of the cottonseed are important not only from the standpoint of the fertilizer requirements of the cotton plant and the value of cottonseed meal as a constituent of fertilizers, but also from the standpoint of the nutritional value of cottonseed meal as a feed and of cottonseed flour as a food. It is rather surprising to find that the best source of information on the mineral constituents of cottonseed is found in a monograph published in 1896.[65] This contains a detailed compilation of the analytical data reported for cottonseed in the early bulletins of the State Agricultural Experiment Stations as well as those from other sources. Although more recent investigators have undoubtedly used more accurate analytical methods, the number of samples on which analyses have been reported are not sufficient to establish either the limits or the average values for the mineral constituents of the cottonseed. Considerable variation in the percentage of the mineral constituents probably occurs as a result of different conditions of growth, soil fertility, and fertilizer ap-

[64] M. Lishkevich, *Masloboino Zhurvoe Delo*, **15**, No. 2, 6–8 (1939).
[65] A. C. True, "The Cotton Plant," *U.S. Dept. Agr. Expt. Sta. Bull.*, **33** (1896).

plication. However, no systematic study appears to have been made of the influence of these factors on the mineral constituents.

The minimum, maximum, and average values for some of the mineral constituents of cottonseed and cottonseed meal are reproduced from *The*

TABLE 155

Mineral Constituents of Cottonseed and Cottonseed Meal[a]

Constituent	Cottonseed, per cent by weight			Cottonseed meal, per cent by weight		
	Min.	Max.	Av.	Min.	Max.	Av.
Moisture	7.04	9.51	8.42	4.34	12.57	7.81
Ash	2.80	4.96	3.78	3.35	9.90	6.95
P_2O_5	0.76	1.77	1.27	1.26	4.62	2.88
K_2O	0.73	1.63	1.17	0.87	3.32	1.77
Na_2O	0.02	0.50	0.20	0.03	0.73	0.29
CaO	0.11	1.15	0.25	0.27	1.25	0.43
MgO	0.40	0.79	0.55	0.48	1.26	0.95
SO_3	0.01	0.27	0.12	0.07	0.40	0.19
Fe_2O_3	0.02	0.13	0.07	0.12	0.19	0.14
Cl	0.02	0.18	0.05	—	—	—
SiO_2	0.01	0.12	0.06	0.02	1.36	0.27

[a] A. C. True, "The Cotton Plant," *U.S. Dept. Agr. Expt. Sta. Bull.*, **33**, 1896.

Cotton Plant in Table 155. These data comprise a summary of the results of 15 analyses of seed and 204 analyses of meal.

The mineral constituents for one sample of cottonseed kernels were determined by McHargue.[13] Although his analyses are quite complete, the results may not necessarily represent either typical or average values. Since they are the only recent data of their kind which are available, they

TABLE 156

Mineral Constituents of Cottonseed Kernels and Their Crude Ash[a]

Constituent	Kernels[b]	Crude ash[b]	Constituent	Kernels[b]	Crude ash[b]
Ash (crude)	4.176	—	Magnesium	0.3778	9.049
Copper	0.0054	0.1278	Phosphorus	1.794	42.96
Iron	0.0150	0.358	Potassium	1.159	27.75
Manganese	0.0013	0.029	Sodium	0.7113	17.04
Zinc	0.0320	0.767	Sulfur (total)	0.361	—
Calcium	0.1858	4.450	Nitrogen	7.52	—

[a] J. S. McHargue, *J. Am. Soc. Agron.*, **18**, 1076–1083 (1926).
[b] Calculated as per cent by weight, on a moisture-free basis.

are reproduced in Table 156. Values are shown for the mineral constituents of hand-separated kernels as well as for the crude ash obtained from them.

The presence of 0.011 to 0.013% of boron has been reported by McLean and Hughes[66] for American upland and Egyptian Sakellaridis cottonseed.

[66] R. C. McLean and W. L. Hughes, *Ann. Applied Biol.*, **23**, 231–244 (1936).

Dahle[34] has reported the presence of 20 to 31 p.p.m. of fluorine in cottonseed meal. Fraps and Fudge [67] determined the iodine content of 235 samples of commercial cottonseed meal produced in different geographical areas of Texas. They found that the iodine content varied from 23 to 1,420 parts per billion. In general, there was good agreement between the average iodine content of the meals and the average iodine content of the soils in the different areas in which the meals were produced. Other analyses for various mineral constituents of the cotton plant have also been reported by White [68] and by Fraps.[69]

Lander and Dharmani [70] have reported data for the mineral constituents of American cottonseeds used as feeding stuffs in India. Their results are in good agreement with those shown in Table 155. They reported the aluminum content on five samples of American and one of Desi cottonseed as ranging from 0.010 to 0.056% and averaging 0.029%, calculated as Al_2O_3.

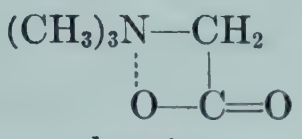
Qualitative spectrographic analysis of cottonseed meal by Allison and Whitehead[71] has revealed the presence of strontium, barium, manganese, nickel, copper, boron, zinc, iron, and aluminum in all samples examined. Vanadium, chromium, molybdenum, and titanium were found in most of the samples—and tin, lead, and yttrium in some.

It is clearly evident that determination of the various mineral constituents of cottonseed by modern methods, including polarographic and quantitative spectrographic methods, on samples of known agronomic history would yield much valuable information. It is of interest to note that agronomic investigations have established that for optimum growth and production the cotton plant requires various minor or trace elements,[72] among which are manganese,[73] copper,[74] boron,[75–78] magnesium,[79] and sulfur.[80]

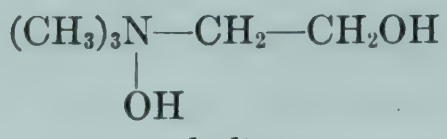
[67] G. S. Fraps and J. F. Fudge, *Texas Agr. Expt. Sta. Bull.*, **595,** 3–25 (1940).
[68] H. C. White, *Georgia Agr. Expt. Sta. Bull.*, **114,** 258–268 (1915).
[69] G. S. Fraps, *Texas Agr. Expt. Sta., Bull.*, **247,** 3–17 (1919).
[70] P. E. Lander and P. L. C. Dharmani, *Indian J. Vet. Sci.*, **5,** 343–349 (1935).
[71] R. V. Allison and T. Whitehead, Jr., *Florida Grower,* **51,** No. 1, 4, 19 (1943).
[72] For an excellent source of information concerning minor element requirements of plants, the reader is referred to L. W. Willis, *Bibliography of Reference to the Literature on the Minor Elements and Their Relation to Plant and Animal Nutrition,* 3rd ed., Chilean Nitrate Educational Bureau, Inc., New York, 1939, and supplements 1 through 6, published annually 1940 through 1945.
[73] Georgia Experiment Station, *Georgia Expt. Sta. Rept.* (*1937–38*), **50,** 62–63 (1938).
[74] W. L. Churchman, M. M. Manns, and T. F. Manns, *Crop Protection Digest, Bull. Ser.* **No. 63,** 26 pp. (1937).
[75] F. M. Eaton, *Soil Sci.*, **34,** 301–305 (1932).
[76] K. T. Holley and T. G. Dulin, *J. Agr. Research,* **59,** 541–545 (1939).
[77] F. M. Eaton, *Botan. Gaz.*, **101,** 700–705 (1940).
[78] W. Schropp and B. Arenz, *Phytopath. Z.*, **12,** 366–404 (1939).
[79] J. J. Skinner, A. R. Knudsen, and E. R. Collins, *Com. Fertilizer,* **65,** No. 4, 8–11 (1942).
[80] O. R. Younge, *Soil Sci. Soc. Am. Proc.*, **6,** 215–218 (1941).

D. Nitrogenous Constituents Other Than Protein

In addition to protein which has been discussed in Chapter VIII and the phosphatides which have been discussed in the chapter dealing with cottonseed oil, two closely related nitrogen compounds are present in cottonseed, namely, betaine and choline whose formulas are:



betaine



choline

Ritthausen and Weger [81] first obtained betaine from cottonseed by treatment of the mother liquor remaining after separation of the carbohydrate, raffinose. Boehm [45] had previously isolated choline in the same manner. Maxwell [82] determined the relative amounts of these two constituents in cottonseed and found the ratio to be 5.7 parts by weight of betaine to 1 of choline.

Betaine is widely distributed in plants, as well as in certain animal tissues, therefore its presence in the cottonseed is not surprising. The method of isolation reported does not preclude the possibility that the isolated choline may have been formed by the hydrolysis of lecithin.

Klinkenberg [83] found that cottonseed cake contained nitrogen compounds which were not digestible by the digestive enzymes present in the stomach of the hog. He concluded that these compounds were "nucleins." However, Jones and Csonka [42] assayed cottonseed meal by chemical methods for nucleic acid, and were unable to isolate it or obtain evidence of its presence. It may be concluded, therefore, that the presence of a nucleic acid in cottonseed meal is not definitely established and, if it does occur, it is probably present only in very small amounts.

E. Antioxidants

By extracting various oilseed meals after treatment with acetic acid in water, acetone, or ethanol, Hilditch and Paul [84] isolated fractions having marked antioxidant activity. The fraction obtained from cottonseed meal showed very pronounced activity, but the compound responsible for this activity could not be isolated or identified. Nevertheless, the authors expressed the belief that it was a basic oxygen compound. In the case of cottonseed, it is possible that this activity may be due to gossypol or related compounds known to possess marked antioxidant activity.

The known antioxidant constituents of most oilseeds are the oil-soluble tocopherols which are discussed elsewhere (pages 381–383). Their

[81] H. Ritthausen and F. Weger, *J. prakt. Chem.*, **30,** 32–37 (1884).
[82] W. Maxwell, *Am. Chem. J.*, **13,** 469–471 (1891).
[83] W. Klinkenberg, *Z. physiol. Chem.*, **6,** 155–165 (1882).
[84] T. P. Hilditch and S. Paul, *J. Soc. Chem. Ind.*, **58,** 21–24 (1939).

activity is enhanced by the presence of phosphatides. The latter substances are therefore classed as synergists rather than antioxidants.

F. Vitamins

The vitamins may be divided into two classes, namely, the oil-soluble vitamins and the water-soluble vitamins. Vitamins A, D, E, and K are oil-soluble, while the various factors composing the vitamin B complex, as well as vitamin C, are water-soluble.[85] In the pressing or extraction process of producing oil from cottonseed, the oil-soluble vitamins generally accompany oil, while the water-soluble vitamins remain in the meal. The oil-soluble vitamins have been discussed in the chapter dealing with the components of cottonseed oil (see pages 377–383), and hence will be treated here only briefly. They are of interest in relation to the feeding value of cottonseed meal, since some of the oil-soluble vitamins are retained in the residual oil which remains in the meal.

1. Vitamin A

According to Fraps and Treichler,[86] cottonseed meal is very low in vitamin A. Halverson and Sherwood [87] found both cottonseed meal and hulls to be deficient in vitamin A precursors when tested as feed for growing cattle. Booher and co-workers [88] found that the carotene present in cottonseed oil was about 50 to 60% as effective as vitamin A in the form of cod-liver oil in preventing deficiency symptoms. Miller[89] claims that the antioxidants in cottonseed meal serve to stabilize vitamin A when the meal is incorporated in mixed feeds containing cod-liver oil. However, intimate mixing of the oil and meal is necessary to obtain this protective action.

2. Vitamin B Complex

The number of compounds in the vitamin B complex constantly increases as new nutritional factors are found. The physiological action of some of these newer factors is not yet clearly understood. A number of the older members of this group as well as some of the more recently discovered factors are known to be present in cottonseed.

(a) Thiamin or Vitamin B_1. Thiamin, or vitamin B_1 as it is now known, was formerly called vitamin B. Cottonseed meal is a good source of this vitamin. Stevens,[90] and also Munsell and DeVaney [91] found that

[85] For information concerning the chemistry and physiology of the vitamins, the reader is referred to: H. R. Rosenberg, *Chemistry and Physiology of the Vitamins,* Interscience, New York, 1945; *The Vitamins,* Am. Med. Assoc., Chicago, 1939.

[86] G. S. Fraps and R. Treichler, *Texas Agr. Expt. Sta. Bull.,* **477,** 3–34 (1933).

[87] J. O. Halverson and F. W. Sherwood, *North Carolina Agr. Expt. Sta. Tech. Bull.,* **39,** 5–158 (1930). J. O. Halverson, E. H. Hostetler, J. E. Foster, and F. W. Sherwood, *J. Nutrition,* **18,** 285–296 (1939).

[88] L. E. Booher, E. C. Callison, and E. M. Hewston, *ibid,* **17,** 317–331 (1939).

[89] H. G. Miller, *Oil & Soap,* **12,** 51–52 (1935).

[90] H. Stevens, *Oil & Fat Ind.,* **7,** 215–216 (1930).

[91] H. E. Munsell and G. M. DeVaney, *Cereal Chem.,* **10,** 287–297 (1933).

cottonseed meal and flour compared favorably with dried yeast as a source of this vitamin. Hunt [92] also has reported that cottonseed meal is a good source of the B complex. Whitsitt [93] found cottonseed meal a good source of B_1, but the cottonseed hulls did not contain this vitamin.

(b) Riboflavin, Vitamin B_2 or G. Cottonseed meal has been reported [90, 91, 93] to be a good source of vitamin G or B_2. Levine and Remington [94] reported that cottonseed contained 2.9 Bourquin-Sherman units per gram of meal. Whitsitt [93] found that cottonseed hulls were also a good source of this vitamin.

(c) Nicotinic Acid. Nicotinic acid or nicotinamide is considered to be the pellagra-preventive factor of the B complex. Sebrell *et al.*[95] have reported cottonseed meal to be a relatively poor source of this factor.

(d) Choline. Choline has been found to be an essential dietary factor and may be considered to be a member of the vitamin B complex. It is present in cottonseed in the form of the phosphatide, lecithin.

(e) Inositol. The dietary significance of inositol has recently been pointed out by Woolley.[96] Inositol is present in cottonseed in the form of phytin. However, since phytin is not readily absorbed in the alimentary canal and is excreted largely unchanged, the inositol which it contains would be available only after hydrolysis by the enzyme phytase.

(f) Other Factors of the Vitamin B Complex. Cheldelin and Lane [97] determined the thiamin, riboflavin, nicotinic acid, pantothenic acid, pyridoxine, biotin, inositol, and folic acid content of cottonseed

TABLE 157

Vitamin B Complex Content of Cottonseed before and after Germination[a]

Factor	Before germination	After germination for 36 hours	Per cent change
Dry material, %	84	53	—
Thiamin	3.2[b]	4.9[b]	+53
Riboflavin	2.3	2.8	+22
Nicotinic acid	16	24	+50
Pantothenic acid	11	22	+100
Pyridoxine	0.91	2.6	+190
Biotin	0.29	0.28	−3
Inositol	3400	2800	−18
Folic acid	3.8	7.9	+110

[a] V. H. Cheldelin and R. L. Lane, *Proc. Soc. Exptl. Biol. Med.*, **54**, 53–55 (1943).
[b] Figures below are micrograms per gram, on a dry-weight basis.

[92] C. H. Hunt, *Ohio Agr. Expt. Sta. Bimonthly Bull.*, **158**, 178–182 (1932).
[93] M. L. Whitsitt, *Ind. Eng. Chem.*, **25**, 1169–1171 (1933).
[94] H. Levine and R. E. Remington, *J. Nutrition*, **13**, 525–542 (1937).
[95] W. H. Sebrell, G. A. Wheeler, and D. J. Hunt, *U.S. Pub. Health Repts.*, **50**, 1333–1341 (1935).
[96] D. W. Woolley, *J. Nutrition*, **28**, 305–314 (1944).
[97] V. H. Cheldelin and R. L. Lane, *Proc. Soc. Exptl. Biol. Med.*, **54**, 53–55 (1943).

before and after germination. Germination for 36 hours increased the content of all these factors except biotin and inositol, which were decreased slightly. The results of their analyses are shown in Table 157. Sherwood and Singer [98] found 0.75 μg. per g. of folic acid in cottonseed. This is somewhat less than was found by Cheldelin and Lane as shown in Table 157.

The fact that many of the B vitamins have been observed to increase during germination [97, 99] of various types of seed would appear to indicate that these vitamins may play an important role in the metabolic processes of the seed.

3. Vitamin D

Cottonseed oil has been shown to acquire vitamin D activity on irradiation with ultraviolet light.[100, 101] However, Halverson and Sherwood [87] have shown that cottonseed meal and hulls do not contain sufficient vitamin D to fully meet the needs of cattle.

4. Vitamin E

Cottonseed oil is a relatively good source of vitamin E (see pages 381–383). Hathaway and Davis [102] found that 20 to 25% of cottonseed meal added to a deficient diet furnished sufficient vitamin E to allow experimental rats to cast litters.

G. Miscellaneous

1. Lactic Acid

Van Kampen [103] isolated lactic acid from cottonseeds as well as from soybeans. It was found to exist in the seed as a trihydrate of the magnesium salt of lactic acid, $Mg(C_3H_5O_3)_2 \cdot 3H_2O$.

2. Saponin

The presence of a saponin in cottonseed meal has been mentioned by Meyer.[104] The fact that nothing further can be found in the literature concerning the nature of this constituent of the cottonseed is in decided contrast to the state of our knowledge regarding the saponins of the soybean.[105]

[98] M. B. Sherwood and E. D. Singer, *J. Biol. Chem.*, **155,** 361–362 (1944).
[99] P. R. Burkholder, *Science,* **97,** 562–564 (1943).
[100] A. F. Hess, *Am. J. Diseases Children,* **28,** 517 (1924).
[101] A. F. Hess, M. Weinstock, and D. Helman, *Proc. Soc. Exptl. Biol. Med.,* **22,** 76–77 (1924).
[102] I. L. Hathaway and H. P. Davis, *Neb. Agr. Expt. Sta. Res. Bull.,* **73,** 3–7 (1934).
[103] G. B. van Kampen, *Biochem. Z.,* **187,** 180–182 (1927).
[104] A. Meyer, *Z. deut. Öl- u. Fett-Ind.,* **41,** 536–538 (1921).
[105] K. S. Markley and W. H. Goss, *Soybean Chemistry and Technology,* Chemical Pub. Co., Brooklyn, 1944.

3. Other Possible Constituents

In concluding this chapter, it may be pointed out that considerable data is available concerning the miscellaneous constituents of the cottonseed. However, many of these constituents merit more intensive and detailed investigations, especially by the application of the more recently developed tools and techniques. In addition, it is quite probable that other, as yet undetected, constituents are present in the seed.

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C. GRADING AND EVALUATION OF COTTONSEED AND ITS PRIMARY PRODUCTS

CHAPTER X

GRADING AND EVALUATION OF COTTONSEED

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I. Introduction

During a period of a little over 70 years, cottonseed has been converted from a very troublesome waste into one of the major cash crops of the southern United States.

Shortly before the Civil War three or four pioneer cottonseed oil mills began the utilization of this waste. The project was interrupted by the war, but was taken up again shortly after the termination of hostilities, and in the year 1875, about 5% of the estimated production of cottonseed was crushed. Originally, the crushing industry was considered to be merely a salvaging industry. For many years it had been the custom for producers generally to abandon the bulk of their seed at the gins, where it accumulated until the ginner was forced by law to dispose of it. At first the price offered for cottonseed bore no relation to the value of the products, but was frequently just sufficient to divert the seed from the refuse pile to the oil mill.

In the year 1885, the crushing industry consumed approximately 500,000 tons of cottonseed, or 19% of the estimated production. By the end of the next decade, the annual crush had grown to over 1.5 million tons, or approximately 35% of the seed produced, as estimated by the Bureau of the Census. The industry had then grown to such an extent that the seed was becoming a large factor in the total value of the cotton crop, and the value of the products of the seed was so great that both the sellers and the buyers of cottonseed became interested in the price paid. As a result, the crushing mills began to examine more closely the quality of the seed they bought, and organized themselves into an association for the purposes of further improving and expanding their business. By the end of the next five years, the industry was crushing nearly 54% of the seed produced.

II. Early Development of Trading Rules and Practices

A. First Trading Rules

The result of the conditions outlined above was the adoption in the year 1899 by the associated cottonseed crushers, of two rules governing the purchase of cottonseed. These rules read as follows:[1]

Rule 1, Section 1. Prime cottonseed shall be clean, dry, and free from dirt, trash, and bolls.

Section 2. Off Seed—Cottonseed not coming up to the requirements of Prime Seed shall be considered Off Seed. Off or damaged seed shall be settled for on its merits and comparative value as against value of Standard Prime Seed.

By the year 1910, the cottonseed oil mills were crushing more than 70% of the cottonseed produced in the United States and the rules for purchases adopted in 1899 were being found inadequate in that they did not describe in definite terms either the nature of "off seed" or how "off seed" should be settled for "on its merits and comparative value."

The definition of prime cottonseed was amended in about 1911 by adding the words,[2] "and must be the fruit of the upland cotton plant." Whether this indicates that other seeds were being mixed with cottonseed or whether it simply was an effort to secure cottonseed free from dirt and trash is not disclosed. Possibly it was designed to discriminate against seed of the Sea Island type (*Gossypium barbadense*), the oil from which, as expressed by the method prevailing at that time, was of lower quality than that from Upland seed (*G. hirsutum*). However, about this time the organized crushers appealed to the U.S. Department of Agriculture for assistance in the establishment of a more definite wording of *Section 2*, relative to "off seed," and to use its influence in stopping the practice of incorporating all types of foreign matter in the seed before delivering them to the oil mills.

B. Rules Based on Discounts for Percentage of Subquality Seed

At the annual convention of the Interstate Cotton Seed Crushers' Association held in June, 1917, the president of the association said in his address:[3]

"Early in the season a special committee from this association took up with Dr. Charles J. Brand, Chief of the Bureau of Markets, the subject of grading cottonseed . . . It is to be hoped that through the medium of this department we may soon have enacted a law providing for government inspection and classification of interstate shipments of cottonseed . . . There is no logical reason why cottonseed . . . should not be classified and graded just as wheat and corn are."

[1] Texas Cotton Seed Crushers' Association, *Trading Rules, 1899.*
[2] Interstate Cotton Seed Crushers' Association, *Trading Rules, 1911,* p. 12.
[3] G. W. Covington, *Cotton Oil Press,* **1,** No. 2, 43–45 (1917).

As a result of the conferences with the U.S. Bureau of Markets and Rural Organization, a method of judging and measuring deterioration in cottonseed was proposed, and after further discussion of the subject the association adopted the following rules:[4, 5]

Rule 2. Section 1. Cottonseed shall be untreated, by either chemical or mechanical process, unless a clear and explicit statement to this effect is made at the time of sale.

Section 2. Deduction at the rate of the delivered price shall be made for all foreign matter in excess of 1 per cent, and for moisture in excess of 10 per cent.

Section 3. Cottonseed shall be graded and settled for as follows:

Grade	Damaged and immature seed, maximum	Settlement basis
No. 1	3%	Premium, 2%
No. 2	6%	Basis
No. 3	12%	Penalty, 3%
No. 4	20%	Penalty, 7%

Sample Grade: All Seed below grade No. 4, according to sample.

Seed which contain in excess of 3% damage, but which do not exceed 6% damage, shall be classed as No. 2 grade. Seed which contain in excess of 6% damage, but which do not exceed 12% damage, shall be classed as No. 3 grade. Seed which contain in excess of 12% damage, but which do not exceed 20% damage, shall be classed as No. 4 grade. Seed which contain in excess of 20% damage shall be sample grade and be settled for according to sample.

Section 4. At least 6 samples of about five pounds each, fairly representing the contents of the car, or two samples of two pounds each, fairly representing the contents of the wagon, shall be taken from various parts of the car or wagon. These samples shall be thoroughly mixed and from this mixture 100 seeds shall be taken at random, which shall be cut in two and the contents graded. All kernels showing color darker than the natural color of seed shall be classed as damaged seed; and all immature seed shall be classed as damaged seed. The percentage of damage shall be determined by counting the damaged and immature seeds. Determination of moisture shall be made in accordance with the official methods of the Chemists' Committee of this Association.

In an address at the Annual Convention of the Interstate Cotton Seed Crushers' Association held in May, 1914, Dr. Andrew M. Soule[6] stated:

"The manufacturer of cottonseed is interested in its viability . . . I think I am correct in stating that weak, indifferent seed does not produce vigorous and effi-

[4] Interstate Cotton Seed Crushers' Association, *Trading Rules, 1917–1918,* pp. 18–20.

[5] See A. D. Hudson, *Cotton Oil Press,* **1,** No. 2, 87 (1917).

[6] A. M. Soule, *Proceedings of the Convention of the Interstate Cotton Seed Crushers' Association, Trading Rules 1914–15,* p. 68.

cient plants which yield the highest grade of lint and seed, lessening its value, therefore, to the farmer and to the seed crusher as well."

It is possible that this statement may have suggested the idea of including "immature seed" in the description of damaged seed or "off seed."

In 1918, the above rules were amended by providing a new settlement basis as follows:[7]

Settlement Basis: Deductions from the delivered price for each percent in excess of 6 per cent of damaged and immature seed to be applied shall be as follows: Grade No. 1 not to exceed 6% damaged and immature, no deductions; Grade No. 2 not to exceed 14% damaged and immature, ½ per cent; Grade No. 3 not to exceed 30% damaged and immature, ⅗ per cent; Grade No. 4, not to exceed 50% damaged and immature, ¾ per cent.

Seed containing more than 50% damaged and immature seed were rejectable and remained so until 1931, when the rejection clause was eliminated and the discount of ¾% of the contract price for each per cent of damaged and immature seed was extended to cover amounts of damaged and immature seed in excess of 50%.

C. Inadequacy of the Discount System

1. Marketing of Trashy Seed

Dr. Brand, Chief of the Bureau of Markets, in his annual report (1917), called attention to the undesirable current practice of marketing cottonseed containing much trash and other foreign matter. Dr. Brand reported that the Bureau had estimated this useless material at approximately 120,000 tons annually and the freight that was paid for transporting it at $200,000. During World War I, the Food Administration issued a rule requiring the separation of foreign matter at the gins and forbidding the returning or mixing of foreign matter either in the process of ginning or afterward. In addition, the U.S. Department of Agriculture, under the Food and Drug Act, declared the mixing of foreign matter with cottonseed to be a violation of the provisions of that act. However, in spite of these prohibitions, foreign matter continued to be incorporated with the seed or was not removed during the ginning.

While the discount rules assessed penalties for the inclusion of foreign material in the seed, the bad practices described above were doubtless attributable in part to a lack of uniform and specific methods for sampling and testing seed shipments.

2. Influence of the Fortuitous Growth of the Industry

The early failure to develop adequate methods for the evaluation of cottonseed and its products is understandable in view of the rapid and

[7] Interstate Cotton Seed Crushers' Association, *Trading Rules, 1918–1919*, p. 17.

fortuitous growth of the crushing industry. The situation can perhaps be best described by a quotation from the address of one of the larger operators,[8] delivered in June, 1921:

"After the Civil War the cotton oil industry got a real start and the demand for cottonseed products was soon greater than the supply. The business grew very rapidly and mills were built hurriedly all over the South. The rush to build mills was so great and the profits from manufacturing so large that very little, or no attention was paid to economy either in erection of plants or in the operation of them . . . The oil mill business is simply repeating industrial history. It, like the other large enterprises which had a rapid initial growth with large profits at first, has now reached the point where the profits must come from efficient operation, supervision, and stable operation. The mills that continue to waste money in the operating departments may expect to lose money on their investment from now on. The time has come when the losses in our manufacturing departments, now so prevalent, must be corrected if the enterprise is to prosper. Our losses are entirely too high and our operating cost all out of proportion as compared with other industries manufacturing commodities. Other large industries such as the paper industry, steel, sugar house, cotton mills, etc., long ago realized the necessity of the assistance of an expert consulting specialist to help them solve their manufacturing problems. So far, the cotton oil industry has never had available this kind of service."

This statement was made at a time when the mills were crushing annually approximately four million tons of cottonseed, or nearly 80% of the annual production of cottonseed.

3. Suggestions for an Improved Basis for Grading

Owing to the lack of funds and loss of personnel in the Bureau of Markets, government investigations on cottonseed grading were suspended in 1920.[9] By this time, however, it was not only generally recognized that "Prime Seed" might vary in value because of differences in the contents of oil and protein, but serious doubts were being expressed as to whether the color of the kernels or the immaturity of seed were directly correlated with crushing problems or with the quality of the products produced in the crushing mills. A committee of chemists was appointed by the Crushers' Association to investigate the question of damaged and immature seed. This committee reported [10] in June, 1921, as follows:

The determination of damaged seeds is very uncertain, as it depends on the personal judgment of the observer. Although very convenient to the seed buyer, it leads quite often to wrong conclusions. The committee is in favor of substituting or supplementing this determination. As long as the Interstate rules of settle-

[8] G. W. Covington, *Cotton Oil Press*, **5**, No. 2, 89–90 (1922).
[9] C. J. Brand, *Annual Report of the Chief of the Bureau of Markets, Fiscal Year Ending June 30, 1920*, p. 21.
[10] J. Malowan, *Cotton Oil Press*, **5**, No. 4, 39 (1921).

ment rest on this determination, it will be necessary for the chemists to make this test, but the more scientific, more accurate, and more practical method is to determine the free fatty acids in the oil.

It was also recognized that no generally approved method for determining the oil content of various oilseeds had been developed and it was suggested [11] that the Interstate Cotton Seed Crushers' Association should set up an Association Laboratory, so that problems of chemical procedure could be solved. This was followed by publication of a statement [12] that the matter had been discussed with the crushers and that it remained to be seen whether the Interstate Cotton Seed Crushers' Association would endorse and agree to finance such a laboratory. But no final action was taken on this proposal, although cooperative work [13] on analytical methods was continued by the Society of Cottonseed Analysts and its successor, the American Oil Chemists' Society. In 1928, an Interbureau Committee was set up by the U.S. Department of Agriculture, under the chairmanship of the author, to establish uniform methods for seed analysis. The methods recommended by this committee, based on chemical analysis of the seed, form the basis of the trading rules now used by the industry.

The idea later current within the industry was that the price offered for seed should be based on the average oil content and that grading should be confined to methods of evaluating different degrees of deterioration. This idea is expressed in a letter from Mr. Louis N. Geldert, Assistant to the President of the Interstate Cotton Seed Crushers' Association, to the U.S. Department of Agriculture under date of February 19, 1924, in the following language:

"Cottonseed differs in value according to percentage of oil content, and of immature and damaged seed and of foreign matter or dirt. Whether the percentage of oil content can be taken into consideration in grading standards is an open question, but the other elements of difference are certainly fundamental. Oil content is, of course, the basis factor always in the mind of the purchaser, as oil is the chief product in value. But assuming a general knowledge of the percentage of oil in a given lot of clean mature seed from a given locality, grown under known weather condition, moisture damage and foreign matter percentages are certainly proper items for allowance in settlements for seed not of contract value."

Mr. Geldert then urged the Department of Agriculture to again undertake a study of the subject. During the Convention of the Interstate Cotton

[11] H. S. Bailey and J. M. Johnson, *Cotton Oil Press*, **1**, No. 11, 33–35 (1918).
[12] E. R. Barrow, *Cotton Oil Press*, **1**, No. 12, 35–36 (1918).
[13] For details of this early work, the reader is referred to the annual reports of successive chairmen of the Damaged Seed and Seed Analysis Committee, including F. B. Porter, J. Malowan, D. C. Picard, and T. L. Rettger, published in the Chemists' Section of the *Cotton Oil Press* and *J. Oil & Fat Ind.*, between 1918 and 1928.

Seed Crushers' Association held in New Orleans in May, 1924, the question of grading cottonseed was discussed. One of the speakers [14] said:

"I think that it is probably the most important single thing that we ought to try to accomplish. We have in the rules now, as you all know, not standards, exactly, but allowances for off-grades. . . Another thing is that we are practically not grading cottonseed. . . If this thing works out and we go on with it . . . we will come gradually to a point where we will be paying for a ton of cottonseed what that particular cottonseed is worth."

D. Early Improvement in Sampling Procedures

As a result of the realization that the so-called grading method that was suggested in 1917 was simply a discounting plan that had proved itself to be inequitable, the Department of Agriculture agreed to send the author to the annual convention of the Interstate Cotton Seed Crushers' Association held in May, 1924, to work with the crushing industry and the commercial analytical chemists interested in cottonseed, with a view to developing an equitable and accurate method of grading.

As a result of this contact, the Interstate Cotton Seed Crushers' Association established a seed-grading committee composed of operators of oil mills and of chemists engaged in analyzing cottonseed and its products, to cooperate and to furnish any assistance that might be required.

Immediately after the work was undertaken it became evident that more adequate rules would have to be established covering the drawing of samples of cottonseed. Among the oil miller, two ideas regarding seed samples seemed prevalent: one, that all cottonseed in any given area of production were approximately of equal value, and therefore it was a matter of indifference how the sample was drawn; and the other, that when and where there was evidence of deterioration or adulteration, that was the occasion and place to draw samples. The first studies undertaken demonstrated that shipments of cottonseed were composed of numerous small lots, frequently varying in their content of oil, protein, moisture, residual lint, and foreign matter, and in the degree of spoilage that had taken place. It was apparent, therefore, that the theory that cottonseed were uniform in quality was erroneous, and that considerable skill was required to secure a representative sample.

In studying the subject of sampling, the industry placed a number of railroad carlots of seed at the disposal of the committee. The method used was to channel through the cars from door to door and from end to end. Pictures were taken of the walls of seed at various points and samples were drawn from various points in each wall. These samples were analyzed individually and the residue was combined, thoroughly mixed, and analyzed for comparison with the individual sample analyses and the average

[14] W. H. Jasspon, *Cotton Oil Press*, **8**, No. 2, 35 (1924).

of those analyses. Special studies were made to determine the extent of percolation or movement of foreign matter through the mass of the seed toward the bottom of the load. Further studies were made of the effect of different methods of loading on the disposition of the foreign matter within the load. As a result, detailed rules for drawing, mixing, and quartering samples of cottonseed were recommended and adopted by the industry.[15]

While these rules were subsequently revised, they incorporated a number of principles that have been retained to the present time. These rules were adopted by the Crushers' Association in 1925, but, with the exception of the mills acting in direct cooperation with the Department of Agriculture were not observed generally by the industry.

E. Variability in Cottonseed Composition

The early studies disclosed a large number of variables in the composition of cottonseed not theretofore reported. The residual fiber content was found to range from about 2.0 to 18.0% of the weight of the seed; the moisture content, from about 6.5 to 20.0%; the protein content, from about 14.0 to 31.0%; the kernel content, from 45.0 to 60.0%; and the oil content of the kernels, from 25.0 to 43.0%.

From a quantitative standpoint, the question now resolved itself into one of correlating these variables, so as to arrive at an index of value.

Since two of the variable products usually constituted less than 15% of the value of the seed, they were eliminated from immediate consideration; these were the residual fiber and the hulls. Attention was centered on the problem of correlating the two remaining variable products—oil, and cake or meal.

F. Evaluation on the Basis of Kernel Content

Since both the oil and the protein are contained in the kernels, and the kernel content was found to vary from 45.0 to 60.0% of the weight of the seed, it was at first believed that a quantitative basis for grading might be developed, if a method could be found of determining quickly and accurately, the kernel content of a lot of seed.[16] A theoretical method of evaluating was worked out[17] and considerable effort was made to develop a machine for kernel extraction. Several machinery manufacturers offered their cooperation, but, after the expenditure of considerable effort and expense by these cooperators, the project was abandoned as being

[15] Interstate Cotton Seed Crushers' Association, *Trading Rules, 1925–1926*, pp. 47–49.

[16] F. B. Porter, *Cotton Oil Press*, **2**, No. 3, 44 (1918); **3**, No. 3, 89 (1919).

[17] G. S. Meloy, *Cotton Oil Press*, **10**, No. 2, 59–63 (1926); *J. Oil & Fat Ind.*, **3**, 209 (1926).

impracticable, since it seemed impossible to make either a complete separation of the kernels or to be assured of constancy in the error.

Moreover, it later developed that the variable residual fiber content accounted for a large part of the variableness of the kernel content, and the greater the fiber content the more difficult was the kernel separation. Further studies of the theory of grading cottonseed on the basis of the net kernel content were suspended, since it did not appear feasible to make accurate physical determinations of the kernel content, which at best would furnish only an estimate of value. Renewed consideration was given to the possibility of making quantitative determinations of the chemical composition of the kernels, which determinations should give an accurate picture of the relative values.

III. Development and Rationale of Present Grading System

A. Methods of Chemical Analysis

A major obstacle to the early efforts to develop a rational grading system for cottonseed was a lack of adequate methods for the chemical analysis of this product. With respect to preparation of the sample for analysis, cottonseed present unique difficulties because of their coating of lint. The lint fibers resist grinding and tend to agglomerate in the ground seed, making it quite impossible for the analyst to reduce a portion of untreated seed to a homogeneous mass.

It was discovered, however, by Malowan [18] that treatment with hydrogen chloride would make the fibers friable and easily ground. The difficult problem of subjecting the seed to the desired uniform exposure to hydrogen chloride without charring portions of the sample was solved by Cox,[19] who adopted the expedient of fuming the seed in an oven with hydrochloric acid absorbed into porous earthenware pots containing the samples. The Cox fuming method was recommended over others by the Seed Committee of the American Oil Chemists' Society [20] in 1926 and is essentially unchanged in the present compilation of official methods. The Malowan principle of acid-fuming, as adapted by Rettger,[21] also forms the basis of the present method for determination of residual lint on cottonseed.

A satisfactory method for another somewhat troublesome determination—that of the free fatty acid content of the oil in the seed—was developed in substantially its present form by Brodie and other members of the Seed Committee of the A.O.C.S.[22] in 1927. The only later modifica-

[18] J. Malowan, *Cotton Oil Press*, **4**, No. 3, 77 (1920).
[19] C. H. Cox, *J. Oil & Fat Ind.*, **3**, 125–127 (1926).
[20] See *J. Oil & Fat Ind.*, **3**, 197–203 (1926).
[21] T. L. Rettger, *J. Oil & Fat Ind.*, **3**, 135 (1926).
[22] R. K. Brodie, *Oil & Fat Ind.*, **4**, 177–181 (1927).

tion of this method was based on two discoveries: first, that in separating the meats from the hulls, the oil from the first meats recovered contains a higher percentage of free fatty acids than the average for the entire sample; and second, that in extracting the oil, the first oil extracted is lower in free fatty acids than the average. These circumstances have made it necessary [23] to make a complete separation and extraction, and not merely to extract "at least 2 g." of oil.

Despite the considerable progress made in the development of analytical methods prior to 1928, the author found in the course of a personal tour of laboratories in the industry that there were no generally used procedures for either sampling or analyzing the seed. Each sampler drew and handled samples more or less according to his own personal ideas, and chemists differed in what they considered proper and accurate methods of analyses. These conditions were reported to the Department of Agriculture, and on December 5, 1928, an interbureau committee was established to develop accurate methods for sampling, handling, and analyzing cottonseed. This committee was composed of Drs. W. W. Skinner, G. S. Jamieson, and J. A. LeClerc of the Bureau of Chemistry and Soils, and G. S. Meloy of the Bureau of Agriculture Economics as chairman.

The Committee reviewed all of the available literature relative to the analysis and composition of cottonseed, and was most fortunate in securing the collaboration of all the commercial chemists who had had cottonseed analytical experience, and also a large number of the chemists employed by cottonseed crushing mills and oil refineries. In all, between 40 and 50 chemists joined in the studies, making suggestions and conducting tests with a view to perfecting the technique required for the accurate analysis of cottonseed and cottonseed oil.

The determination of the free fatty acid content of the oil in the seed presented one of the most interesting and difficult problems. Deterioration of the oil in the seeds apparently proceeds independently in individual seeds. The determination of the free fatty acid content of a sample, representing as it generally does from 20 to 30 tons or more, must necessarily be therefore the average free fatty acids content of all of the individual seed. Two hundred grams of cottonseed are composed of between 1,350 to 2,700 individuals, the oil in each of which will have broken down independently and perhaps to different degrees. For the purpose of free fatty acid determination, the Committee recommended that this sample should be dried, so that the seed coats could be broken and the meats or kernels separated from the hulls. The breaking down of the oil is apparently coincident with physical changes, so that usually the greater the deterioration in the oil, the more friable the seed; therefore, if considerable care is not exercised in the cracking and separation, meats from

[23] R. S. McKinney and G. S. Jamieson, *Oil & Soap*, **11**, 191–192 (1934).

sound seed will not be represented. On the other hand, in the seed, free fatty acids are apparently less soluble than neutral glycerides, so that unless care is taken to recover all of the oil, the higher free acid oil will not be properly represented.[23]

A preliminary report of the work of the Interbureau Committee was made by Dr. G. S. Jamieson [24] at the Annual Convention of the American Oil Chemists' Society in New Orleans in May, 1930. This publication of the recommended analytical procedures and their adoption by the National Cottonseed Products Association, enabled the Committee to secure the benefit of the practical application of the technique involved over a period of two seasons during which time two or three minor changes were found to be necessary and were included in the Committee's final report.[25]

B. Methods of Sampling

At the time that the above-mentioned Interbureau Committee was organized, not only was it recognized that the basis of discounting seed was inaccurate and misleading, but it was also appreciated that the method of drawing samples did not yield a representative sample, and another special committee was appointed to study this subject.

The studies conducted by this committee developed the following facts and conclusions. Cottonseed as loaded into railroad cars is composed of the various small lots of seed recovered in the ginning of individual bales of cotton. These individual lots of seed contain varying quantities of foreign matter, such as sand, dirt, leaves, sticks, stones, pieces of metal, and broken and whole carpels or boll shucks. They are variable in moisture content, and because of differences of variety, soil, climate, and other conditions of growth and harvest, contain various quantities of oil, protein, residual fiber, and hulls.

Loading of the seed is accomplished either by hand or by means of pneumatic or mechanical elevators and conveyors. Hand loading may result in a fair distribution of the variables throughout the car or, consciously or unconsciously, may result in deception or false packing. Pneumatic loading tends to concentrate some forms of foreign matter at eddy points within the car. Cars loaded by this means are frequently so completely filled as to prevent entry for drawing samples, unless the load is first channeled. There is practically no shifting or infiltration of foreign matter during transit.

Cottonseed containing more than 12% moisture is liable to spontaneous heating in transit. The presence of certain foreign matter is conducive to and intensifies the rate of heating. Heating may proceed to the point of

[24] G. S. Jamieson and R. S. McKinney, *Oil & Fat Ind.*, **7**, 291–293 (1930).

[25] The amended report of the committee recommending methods for the analysis of cottonseed is to be found in Association of Official Agricultural Chemists, *Official and Tentative Methods of Analysis*, 5th ed., 1940, p. 443.

charring or actual combustion of the seed. It stops enzymic reaction, so that the development of free fatty acids is arrested. Heating may cause a discoloration of oil, cake, hulls, and linters.

In studying the problem of sampling carlots, trenches were dug in several directions through a number of cars and the walls of the trenches were examined to determine the distribution of the contents, with small samples being taken at various levels and positions in each car. These samples were analyzed individually and collectively. As a result of these studies, it was determined that, as a rule, a sample of less than 50 pounds would not be representative of a car, and that a sample of this size should be made up of portions drawn systematically from various positions in a car.

The sampling of cottonseed in carlots before unloading presented some peculiar problems. Cottonseed do not flow readily, but tend rather to agglomerate or pack, even to the extent that if a rod is inserted into a mass of seed and is then withdrawn, the hole will remain, even after considerable agitation of the seed. A trier, such as that used for grain, therefore, could not be used. The common practice was to trench or channel from the entrance to the center and from the center toward each end of a car. From the walls of this trench, portions were taken by hand; such a procedure was costly and slow.

The characteristics desired in a trier were: ease of insertion and extraction; minimum weight compatible with durability; maintenance of the position of the material during insertion and extraction; and ability to grasp a cross section and withdraw it unaltered.

1. Design of the Cottonseed Trier

A large number of experiments were conducted with augers, punches, shallow trenches combined with digging holes, etc. The first successful trier for cottonseed took the form of an enlarged crowbar with exsertable curved fingers along its sides. After thrusting the bar into the mass of the seed, a crank was turned which caused all of the fingers to protrude and to grasp a cylindrical column of seed. The trier was then withdrawn and the seed released by retracting the fingers. This trier weighed approximately 20 pounds and was costly.

Finally, a simple tool in the shape of a cork screw, made of steel rod bent to form an open cylinder about 4 inches in diameter, was found to give excellent results. This instrument could be used by common labor. However, two sources of possible error were discovered: one, that if turning is continued after the trier reaches the floor, a churning of the contents results with a possible misplacement or change of contents; and two, that the lower part of load could not be sampled without first digging holes.

The present model of the trier is made of strip steel measuring ½ by

5/32 inch in cross section. The inside diameter of the coil is 2½ inches, and the pitch of the screw is 2 inches on centers. The length of the coil is from 4 to 4½ feet. The operating head is provided with a cross-bar handle or with a carpenter's brace for quick insertion. The coil, being made of flat metal, clears the walls in turning, so that no churning of the contents occurs (see Fig. 117).

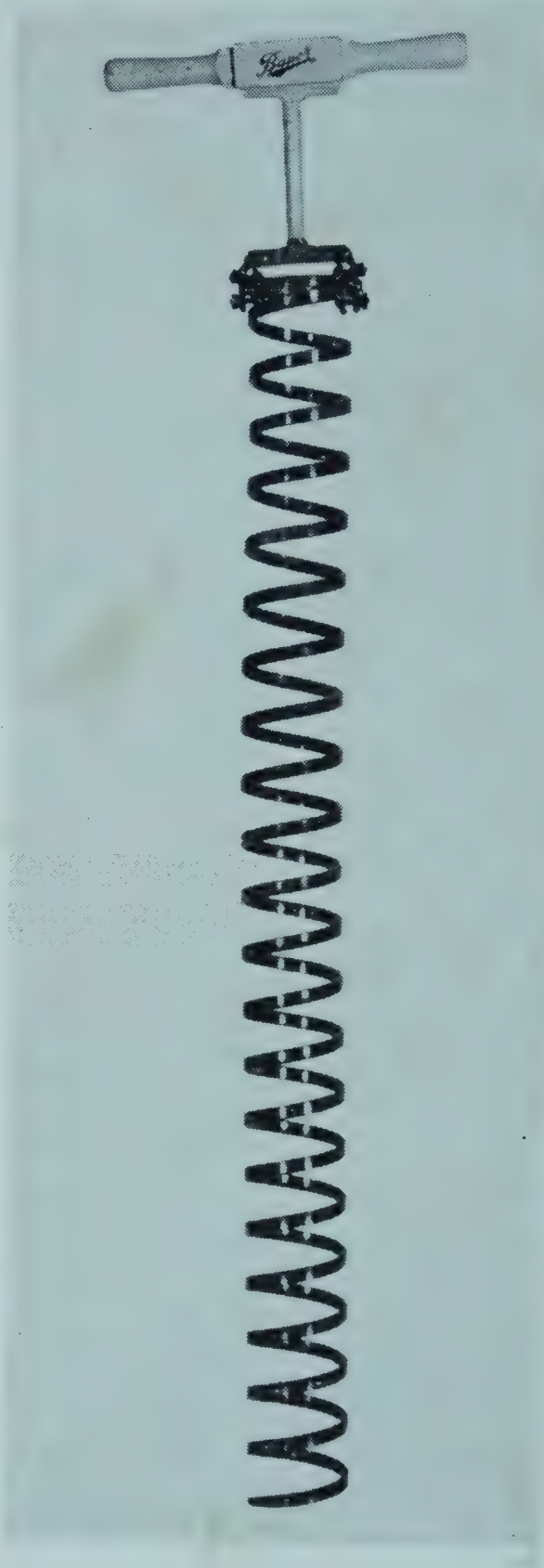


Fig. 117. Official cottonseed trier.

The size of the trier that was devised was fixed with the idea of securing 50 pounds as a result of 10 probes, making 4 probes in each end of the car and 2 in the middle or between the doors.

2. Sampling during Unloading

In sampling a carlot of cottonseed during unloading, the usual practice was to hang a gunny sack on the side of the door and instruct those unloading to place a small shovelful or a few handfuls of seed in the sack from time to time. This involved an extra duty on the part of a laborer—who was engaged in the major operation of throwing large scoopfuls of seed out of the car—to remember to stop more or less regularly and gather portions of a sample. In practice it was found that stops were usually made when some peculiar condition of the seed attracted the eye. It was believed, therefore, that most of the samples so drawn were biased and not representative.

During unloading, whether by hand or machine, the seed are ejected from the car over a funnel-shaped chute. It was suggested that a cross section of this stream of seed, taken either mechanically or at regular intervals by an employee whose first duty was that of sampling, might give a representative sample. Samples drawn in this manner have been compared with samples from the same carlot drawn with the trier before unloading and have checked satisfactorily. For the purpose of sampling during unloading, a 5-inch elevator bucket was attached to the end of a broom handle, forming a receptacle capable of being passed through the

stream of seed and withdrawing approximately two pounds. By presenting such a receptacle at regular intervals—not less than once for each ton of seed in the car, and in no case less than 25 times—the full 50-pound sample is secured, and each ton will be properly represented.

Satisfactory sampling of wagon and truck lots can be accomplished if the procedure for sampling carlots is followed, that is, if the sample is composed of several portions taken from various places with the approved trier and approximates two pounds per ton of seed sampled.

3. Preservation of Samples

The gathering of samples in gunny sacks, the exposure of such sacks to the weather, and the transference of the sacks to the office or other assembly point, there to be left for a convenient time, involved not only the possibility, but the probability of changes in moisture and foreign matter content. It was therefore recommended that metallic containers with close-fitting covers be used.

4. Subdivision of the Sample

(a) Division of the Original Sample. Having drawn from a carlot a representative sample weighing 50 pounds or more, the next problem is that of mixing and quartering it down to a size sufficient for laboratory purposes with assurance that the laboratory portion is as representative as the original sample.

Original samples contain almost every type of substance foreign to seed, such as dirt, sand, stones, leaves, sticks, whole and broken bolls, nuts of all kinds, and various iron objects. It is obvious that such foreign matter cannot be mixed and quartered in its relative proportions. It was, therefore, found necessary to clean the sample before attempting to mix and quarter it. The Committee made the following recommendations. First, that cleaning be done over shaker screens. This procedure offers an opportunity to make only a preliminary determination of the foreign matter content of the shipment, since some of the finer and more scabrous forms of foreign matter are very difficult to separate from the seed. The full sample should therefore be immediately weighed, then cleaned, and the cleaned seed should be weighed. From these weights, the weight of the foreign matter removed can be learned and reduced to a percentage. Since some moisture and dust may be lost during the cleaning process, the calculations should not be made from the weight of the foreign matter that it may be possible to collect.

Individual cottonseeds differ from one another in many respects, such as in size, shape, amount of residual fiber, specific gravity, moisture content, maturity, amount of deterioration, and degree of oil and protein

elaboration, all of which tend to render it difficult to reduce the sample properly.

The usual method of mixing and quartering a sample of material is to place the material on a table top or a large piece of paper, to mix it by passing the fingers or a suitable instrument up through the mass, then to flatten the pile and partition it into four quadrants. Opposite quadrants are reassembled, mixed, and again quartered, until opposite quadrants taken together are of the right size for analysis. When using this method with cottonseed, it was demonstrated that two like portions could seldom be secured. In fact, when mixing is attempted by any of the ordinary methods, a separation and segregation of the several types and qualities frequently results.

In the research work it was necessary, therefore, to devise a mixing and a quartering method by which a sample of 50 or 100 pounds of seed could be reduced to 45 to 50 similar and equal portions, and to devise a method by which a single portion could be quartered from the original sample that would be representative of the whole.

The first problem was solved by modifying the baffles in a revolving-drum MacLellan Mixer so as to make this device applicable to cottonseed, and determining the proper speed and optimum number of revolutions necessary for thorough mixing of the sample. After being mixed, the contents are dumped into a box or in a pile from which, if handled without disturbing the mass, as many separate portions may be lifted as may be desired.

For ordinary commercial purposes, the original 50-pound sample may be cleaned and a representative cross-section portion secured automatically by means of an adjustment placed on a regular shaker-screen cleaning apparatus. The procedure recommended by the Committee for using such a device was that, after being weighed, the sample be placed in a hopper that is equipped with a device for distributing its contents evenly and regularly on to the upper end of the screen. The cleaned seed are collected at the lower end of the screen in a chute through which they pass into a receiving box. An adjustable vent should be installed either at the lower end of the screen or in the side of the chute, through which a cross section of the seed may escape. This portion should be promptly placed in a friction-top can, which has been tared, and immediately closed. To calculate the foreign matter loss, all of the clean seed, including the laboratory portion, should be weighed.

(b) Size of Minimum Laboratory Sample. The question naturally arose as to how far subdivision of a sample may safely be carried out in the case of such a gross and variable material as cottonseed. This question is coupled with the uses to be made of the portion sent to a laboratory. Laboratory requirements are: first, a reserve or referee portion; and

second, separate portions for each of the following chemical determinations: moisture, oil, ammonia, and free fatty acids—each determination to be made in duplicate, and in triplicate unless the duplicates check within certain limits.

A number of experiments demonstrated that a sample of cottonseed, except under conditions of unusual uniformity, could not be quartered to less than 60 g. With this as a basis, it was calculated that approximately 500 g. would be necessary for laboratory purposes, and an equal quantity would be necessary for reserve or referee purposes. The size of the sample to be sent to a laboratory for analysis was therefore placed at 1,000 g. or 2¼ pounds, which is approximately two full quarts.

(c) Reduction of the Sample in the Laboratory. The skill of laboratory assistants is usually of a type that assures sufficient care in the quartering of samples to guarantee representativeness, but considerable time is consumed in the process, and human frailties sometimes contribute to errors. An effort was made, therefore, to find an automatic divider capable of yielding representative portions as small as 60 g. The small-size MacLellan Mixer, Model 00-S, was eventually adopted, since it was found to be accurate, rapidly operated, and easily used by unskilled labor.

Since a sample of cottonseed in its natural state cannot be reduced to less than 60 g. and, since this quantity is too great for practical chemical analysis, it is necessary to grind the sample to a homogeneous mass before proceeding with its analysis. However, as mentioned previously, grinding can be accomplished only after the residual lint fibers are rendered friable by treatment with hydrogen chloride. The fineness of the grinding bears a direct relation to extraction of oil. If too coarse, penetration of solvents is imperfect; if too fine, solvents tend to channel; moreover, the heat developed during grinding may affect the oil, rendering it less soluble, or may cause other substances, such as resins, to become soluble, and thus make the quantitative determinations of oil inaccurate. Proper and improper grinds may be recognized by experienced analysts from the color of the sample.

C. Establishment of Indices of Value

1. Inadequacy of Oil Content as a Sole Index of Value

For many years the oil was the major and principal product of cottonseed; linters were not recovered, cake and meal were by-products, and hulls were a waste. As a legacy of these conditions, oil is still considered the dominant factor in the evaluation of cottonseed, even though the value of the meal recovered per ton of seed is generally fairly close to that of the oil; and on some occasions, the value of the recovered meal per ton of seed has been greater than the value of the oil.

The basing of value on the oil content alone appeared indefensible.

not only because of the variable composition of seed, which sometimes resulted in yields of cake that fully offset deficiencies in oil, but also because of the fact that market conditions might give the cake a value approaching that of the oil. In 1897, the total value of the cake and meal produced per ton of seed was 24.0% more than the total value of the oil produced. The value of the cake continued to exceed the value of the oil in the two succeeding years and again exceeded it in 1906, although in recent years oil has generally been the considerably more valuable product (see page 659).

2. Relative Values of Products. Cake–Oil Value

Price studies showed that the ratio of value of cottonseed oil to cake or meal varied from 1 pound of oil to 4 pounds of 41.15% protein cake, to 1 pound of oil to 6 pounds of cake. The average ratio was approximately 1 to 5.

During a conference between members of the Seed Analysis Committee and the author, it was suggested that a suitable index of value might be based upon this ratio, and a table [26] was prepared in which the total oil and protein had been converted into an oil equivalent. This table was compiled by calculating the number of pounds of oil contained per ton of seed and adding one-fifth the number of pounds of meal of a definite protein content. The calculations were based on the analyses of the seed, and represented the theoretical total pounds of oil and meal. The quantity of meal was calculated on the basis of 41.13% protein content.

To calculate an index, it was necessary to establish a base or average analysis of cottonseed. However, the value of seed analysis had only just begun to be appreciated and only a few chemists had done any volume of this type of analysis. These were located in what was considered the best oil-producing sections of the Cotton Belt and their work was largely confined to testing the oil content of the seed produced in those sections. The first analytical averages were therefore tentative. They were derived from records that showed an average oil content of approximately 19.0% and an average ammonia content of about 3.70%, of which 0.20% was in the hulls and therefore largely eliminated in the hulling, leaving 3.50% available for meal.

Nineteen per cent oil indicates 380 pounds of oil per ton of seed, and 3.50% ammonia indicates 875 pounds of 8.0% ammonia or 41.13% protein meal. One-fifth of 875 is 175, which added to 380 gives a total oil equivalent or "cake–oil value" of 555 pounds.[27]

[26] This table, for which Mr. C. H. Cox, of the Barrow-Agee Laboratories, was responsible, was first published in the Trading Rules of the National Cottonseed Products Association, for 1928–1929, pp. 123–132, with an accompanying explanation of the new evaluation system.

[27] For further details of the method of calculation, see the reference cited in footnote 25.

By dividing a similarly secured figure, calculated from the analysis of any lot of cottonseed by the base figure of 555, a relative value or quantitative index could be secured.[28] This method of evaluating cottonseed was called the "oil–cake reciprocal method."

3. Quality Discounts

The quality of cottonseed, from a crushing standpoint, is affected by the moisture content, the presence of foreign matter, and the relative decomposition of the oil and protein. Moisture content had always been looked upon as a natural condition. Furthermore, since variations in moisture cause an inverse change in both the oil and ammonia contents and therefore in the quantity index, it was thought at first that such quantity index changes would amply reflect quality changes that might result from excesses of moisture.

Foreign matter was considered simply as excess weight, and provision was made to deduct the weight of foreign matter from the gross weight of a shipment of seed and to charge the freight back to the shipper.

Protein deterioration apparently occurs infrequently. When it does occur, it is evident by the loss of ammonia.

The cause of the discoloration or darkening of the kernels has not been determined definitely. The discoloration may appear as spots or as a general brownish tinge or stain. The spots may be the result of the decomposition of the resin glands residing throughout the kernels, whereas the general brown staining is probably the result of the caramelization of the carbohydrates or pentosans during heating in storage, usually as a result of the presence of excessive moisture.

Discoloration of both the oil and cake may occur during the cooking of meats high in carbohydrates, particularly if they are low in moisture through caramelization of the pentosans.

No provision for measuring the reduction in quality of the protein was attempted, since the loss of ammonia would be reflected in the quantity index. The reduction in value per ton on seed due to any change of color in the kernels is usually nominal.

Deterioration of cottonseed oil usually takes the form of liberation of fatty acids, so that the percentage of free fatty acids in an oil indicates the relative deterioration of that oil. Based on the records of the refining of oil produced chiefly in the Mississippi Valley, a table of oil-refining losses was correlated with various percentages of free fatty acids.[29]

The table of losses due to free fatty acids was combined with the cake–oil value to derive a table of relative values.[30]

It was assumed that this table of relative values would establish pre-

[28] G. S. Meloy, *Cotton Oil Press,* **13,** No. 2, 43–48 (1929).
[29] In this connection, see the references cited in footnotes 22 and 25.
[30] G. S. Meloy, *Cotton Oil Press,* **12,** No. 1, 24–39 (1928).

miums for seed having a value above 100 and conversely would establish discounts for seed having a value less than 100. This method of determining the relative values of cottonseed, known as the oil–cake reciprocal method, was recommended for study by the industry in May, 1928—and, with slight changes, was approved for trial by the N.C.P.A. in May, 1929.

4. Average Oil Content of Cottonseed

The recommendation that cottonseed be graded on the basis of chemical analysis was followed to a greater or less extent in almost all states in which oil mills were located. To check the analysis and grading, as well as to secure data for study, chemists were requested to forward copies of all grade reports to the Bureau of Agricultural Economics. The Bureau thereby secured data on a large number of samples of cottonseed representing practically every section of the Cotton Belt. From the information obtained during the season 1930–31, the average oil content of all samples was calculated as 17.86%, which when weighted by the production of seed in each state, gave a weighted average of 18.00% instead of 19.00%, the previously estimated average. The result of using the higher figure, 19.00%, had been to cause an undue proportion of deliveries to fall on the discount side of the base. As the season of 1930–31 was a drought season over a large part of the Cotton Belt, again as a trial figure, the average oil content was assumed to be 18.50%. This necessitated a change in the basis for determining the quantitative index. Eighteen and one-half per cent oil indicates an oil content per ton of seed of 370 pounds, which

TABLE 158

Average Oil Content of Cottonseed Analyzed during the Seasons of 1934–35 to 1937–38[a]

State	Number of samples analyzed	Average percentage of oil
Alabama	17,424	18.24
Arkansas	50,484	18.21
Georgia	20,138	18.61
Louisiana	17,918	18.96
Mississippi	85,712	18.80
North Carolina	8,439	18.88
South Carolina	14,807	18.22
Tennessee	21,080	18.16
Total	236,002	*Over-all average* 18.54

[a] G. S. Meloy, *Variations in the Composition and Grade of Cottonseed Produced in the States of Arkansas, Louisiana, Mississippi, and Tennessee, Seasons of* 1934–35 *to* 1937–38, Mimeographed Circular, U.S. Dept. Agr., June, 1939; *Variations in the Composition and Grade of Cottonseed Produced in the States of Alabama, Georgia, North Carolina, and South Carolina, Seasons of 1934–35 to 1937–38*, Mimeographed Circular, U.S. Dept. Agr., October, 1939.

when one-fifth of the 8.0% ammonia cake yield is added, gives a base figure of 545 instead of 555.

During the three seasons 1930–31, 1931–32, 1932–33, copies of the analysis and grading reports on samples representing more than 135,000 shipments of seed were received, with each sample representing an average of approximately 26 tons. Calculated from these data, the average oil content, when weighted by the production of seed in each state, was 18.54%.

This figure was confirmed by the average oil content calculated from analysis reports received during the four seasons of 1934–35 to 1937–38 (see Table 158).

5. Present Quantity Index

(a) Simplification of Method of Calculation. The oil–cake reciprocal method of finding a quantitative index was somewhat complicated, and therefore invited argument in its practical and general application. However, it could be calculated that a change of approximately one-fourth of one per cent in the oil content, when the ammonia content remained constant, resulted in a unit change in the index; and similarly, that when the oil content remained constant, a change of one-sixth of one per cent in the ammonia content resulted in a unit change in the index. These facts led to the adoption of the following simplified formula [31] for calculating a quantity index directly from the percentages of oil and ammonia found by analysis: 4 times the percentage of oil, plus 6 times the percentage of ammonia, plus 5, equals the quantity index. The constant, 5, that was added was considered as representing the average value ratio of the linters and hulls, and offered a term that could be changed when and if data relative to the importance of variations in the residual fiber content of cottonseed indicated the advisability of such action. The use of this formula gave results comparable with quantity indices derived from the original method within ±0.2–0.3 unit.

(b) Distinction between Normal and Abnormal Seed. In the normal development of cottonseed, apparently the elaboration of the contents are initiated in the following order: carbohydrates, protein, and oil. The normal oil content may vary from about 17.0 to 23.0% on a 10% moisture basis, depending upon the variety of seed and cultural methods, and upon soil, moisture, and other growing and cultural conditions. The slowing up or arresting of the regular and full development of the seed is first apparent from the meager supply of oil that has been elaborated.[32]

The sequence in the elaboration of the constituents of the kernels and the possibility that the elaboration of any one of them may be interrupted

[31] The use of such a formula was first suggested by A. S. Richardson.
[32] G. S. Meloy, *Cotton and Cotton Oil Press*, **44**, No. 23, 14–16 (1943).

or may proceed at various ratios due to different stimulating causes doubtless accounts for the wide range in the composition of cottonseed that is found on analysis.

Analyses of normal seed as compared with analyses of seed grown under adverse conditions, such as prolonged drought, indicate that inhibition of the elaboration of one constituent may result in giving the other constituents an unbalanced position in an analysis. For instance, in seed that normally would elaborate 19.0% oil and 3.57% ammonia, if the elaboration of oil alone were arrested for any cause at 13.0% and the same total quantity of ammonia had been developed, then the ammonia would be calculated as 3.84%. Possibly, the failure to fully elaborate oil is coincident with failure in the development of the structure of the kernels, since the difficulties of processing cottonseed and recovering the products progressively increase with the poorer development of the seed.

To recognize these deficiencies in products on a progressive basis, it was therefore necessary to develop a correction factor for finding the quantity index of subnormal seed, that is, seed in which less than 17.0% of oil is present. The formula for calculating the quantity index for seed containing less than 17.0% oil was accordingly revised to read: 5 times the percentage of oil, plus 6 times the percentage of ammonia, minus 12, equals the quantity index. This formula gives a quantity index lower by one unit for each 1% of oil less than 17.0% than that found by the formula for normal seed.[33] This formula was later amended; for the formula presently in effect (1946), see page 521.

6. Quality Index

(a) Discounts for Foreign Matter. The old rule of the industry, requiring the deduction of the weight of the foreign matter from the gross weight of the shipment and charging the freight back to the shipper, did not fully deter the shipper from the practice of incorporating foreign matter with the seed, nor did the laws and regulations under the Pure Food statute making it an offense to put foreign matter into cottonseed. It may be pointed out that foreign matter constantly accumulates in the handling and transit of seed shipments. The freight charges on such foreign matter when shipped with seed may be less than the cost of cartage. At any rate, the fact remained that much seed, on receipt by the purchaser, contained foreign matter. Its presence stimulated deterioration of the seed itself, and the removal was difficult and costly. It was thus necessary to include the content of foreign matter as an element of grade.[33] Consequently, foreign matter in excess of 3.0% was made a factor in a new, so-called *Quality Index,* the base index of 100 being reduced one unit for

[33] U.S. Department of Agriculture, "The Official Standards of the United States for the Grading, Sampling, and Analyzing of Cottonseed Sold or Offered for Sale for Crushing Purposes," *Service and Regulatory Announcements,* No. 133, August, 1933.

each 1% excess. The present discount, established in 1945, is 0.1 unit for each 0.1% foreign matter in excess of 1.0%.

(b) Discount for Excess Moisture. Excess moisture in cottonseed is caused primarily by inclement weather, but frequently is due also to improper handling by the producer or shipper, or both. In any case, the purchaser suffers when shipments contain moisture in excess of 12.0%. Such shipments usually heat in transit. If stored after arrival, wet seed quickly ferment, heat, and decompose; and the removal of excess moisture from cottonseed is difficult and expensive. For these reasons, excess moisture was included as a factor in the Quality Index of the official standards, and 12.0%, the apparent turning point, was established as a tolerance.[33] The present discount (1946) is 0.1 unit for each 0.1% moisture in excess of 12.0%.

(c) Factor of Free Fatty Acids Content of the Oil. As indicated previously, the old discount system of grading cottonseed, based on a count of damaged and immature kernels, fell into early disfavor. The industry soon appreciated the fact that neither the presence of aborted seed nor the color of the kernels of developed seed had any direct relation to the actual value of the oil, and that only to a limited extent did it affect the value of the cake. It had also came to realize that deterioration in the oil is directly indicated by the amount of free fatty acids present in the oil.[34] Through the cooperation of some of the chemists and crushing mills, the Department of Agriculture secured complete analyses of some 3,000 shipments of cottonseed. These analyses covered the percentages of oil, ammonia, moisture, foreign matter, and "damaged seed" based on the color of the kernels, and also the maturity of the seed and the percentage of free fatty acids in the oil in the seeds. The highest "damaged seed" content reported was 98.0%, and the highest free fatty acid content was 9.6%.

The old rule of the industry covering damaged seed provided a tolerance of 6.0%. Another rule of the industry covering the sale of oil provided a tolerance of 9.0% refining loss in prime crude oil, and it was generally believed that this loss corresponded to about 2.0% free fatty acids in the oil.

When an analysis of the data was made, it was found that 51.0% of the samples were rated as sound, on the basis of the color of the kernels and maturity of the seed; but in 35.2% of these "sound" samples deterioration had taken place in the oil, and in some instances the deterioration was serious. Of the "unsound" 49.0% that were found to contain above 6.0% "damaged seed" (with the damage ranging up to 98.0%),

[34] For the first exhaustive report on the correlation between free fatty acid content of the oil and refining loss and refined oil color, see the article by R. K. Brodie cited in footnote 22.

one-fourth of these shipments were not actually deteriorated, that is, the free fatty acids content of the oil was less than 2.0%. The shipment reported as 98.0% damaged seed was found to contain less than 4.0% free fatty acids in its oil, which was lower than the acidity of some of the shipments that were reported as prime on the basis of so-called damaged seed.

When all of the analyses showing 2.0% or more free fatty acids in the oil were segregated and arrayed in sequence of increasing acidity, it was found that nearly 39.0% of the shipments reported as prime on the basis of the maturity and color of the kernels, had actually deteriorated. A graph of the data did not indicate even a similarity of trend between the so-called damaged seed and the free fatty acids content of the oil.

In connection with the immature and aborted seed it was found that such seed seldom reached the huller, since they were usually moted out in the delinting machines, and therefore they could not possibly influence the quality of either the oil or the cake. Such seed apparently were included in the category of damaged seed simply because the sample used for analysis was too small to place them in their true position, as either excess hulls or foreign matter. Based on these studies, it was determined that there was no scientific basis for measuring deterioration by a count of the number of aborted seeds and seeds with discolored kernels. These facts were reported [35] to the crushing industry at its annual convention of 1927 and gave rise to an intensification of the study of the relation of free fatty acids in the oil to the quality of the products.

Numerous tests developed the fact that the free fatty acids content of the oil in the seed bore a direct relation to the value of the oil produced from such seed. The bulk of the data available for these studies was developed from seed produced under the conditions of growth obtaining in the Mississippi Valley. Cottonseed oil of the type produced in the Mississippi Valley generally refines with a loss of within 9.0%, when the oil contains not more than 2.0% free fatty acids. Based on the yields of products from such seed, figures representing reductions in the value of the oil were converted into percentages of value of the seed. From these data, a curve was made showing the percentage of reduction in the value of cottonseed in relation to increases in the free fatty acids content of the oil. The curve showing the reduction in the value of seed in relation to increase in free fatty acids proved to be nearly a straight line corresponding to 3.5% or 3.5 units for each 1.0% of free fatty acids above 2.0%.

The suggestion that a 3.5% reduction be made on account of each increase of 1.0% in the free fatty acid content met with considerable protest from a number of oil mills as being excessive, and as a compromise

[35] G. S. Meloy, *Oil & Fat Ind.*, **4**, 307–314 (1927).

3.0% was adopted for trial purposes. Almost immediately after the opening of the crushing season, however, the mills began to protest that the rate was, in fact, too low, that deterioration of products other than oil had not been considered in it, and that oil produced under Mississippi Valley conditions differed from the oils produced in other sections of the Cotton Belt.

Further studies were immediately undertaken in which it was found that coincident with deterioration of the oil and increases in the free fatty acids, deterioration took place in the quality of the other products. An effort was made to combine the reduction in quality on all products and to convert the combined loss into percentage of the value of seed. The curve of these combined losses was somewhat irregular, but averaged approximately 5.2% of the seed value for each 1.0% increase in the free fatty acids content above 2.0%. Further evidence was also gathered on the breaking point between the free fatty acids content and the reduced value of oil. The more general data secured indicated that the breaking point between prime and off oil occurred more frequently below 2.0% free fatty acids than at 2.0%. The modal point for oils produced in all sections of the Cotton Belt apparently was 1.8%. As a consequence of the above studies, 1.8% was set as the maximum free fatty acids content for prime seed, and reductions were made in the quality index at the rate of 0.5 unit for each 0.1% free fatty acids above 1.8%. The present discount, established in 1945, is 0.4 unit for each 0.1% above 1.8%.

In a test run made on 1,800 tons of cottonseed, in which samples of seed were drawn as the seed were passing into the processing operations, the seed were carefully and promptly processed, and samples of the products were immediately drawn—a rate of 5.0% of the seed value for each 1.0% increase in free fatty acids proved to be accurate with a plus of 3.8 cents per ton of seed on a base price of $36 per ton.

7. Present Grade Standards

In the early spring of 1932, the Interbureau Committee made its report recommending a method of grading and also methods for the sampling and chemical analysis of samples of cottonseed. The recommended methods of grading, sampling, and analyzing cottonseed were promulgated on May 23, 1932 by the Secretary of Agriculture, as one of the official standards of the United States.[33]

From time to time the original grades have been amended so as to meet unforseen variations in the composition of cottonseed and improvements in the methods used in harvesting, ginning, and handling, as well as in the processing of cottonseed. The objectives of the amendments have been to maintain, as far as possible, a fair and equitable spread between the price of a grade and the value of the products obtainable from that

grade, and at the same time to simplify the language of the standards. One of the first amendments covered the grading of cottonseed of extreme and unusually low oil content. The last amendment took advantage of the improvement in the storage facilities and in the practice of better methods of oil milling, which resulted in improvements in the quality of the crude oil produced, and therefore permitted a reduction in the rate of discount on account of excesses of free fatty acids in the oil.[36]

The standards for grades of cottonseed sold or offered for sale for crushing purposes as amended June 4, 1945 [36] are as follows:

§ 28.401 *Determination of grade.* The grade of cottonseed shall be determined from the analysis of samples, and it shall be the result, stated in the nearest whole or half numbers, obtained by multiplying a quantity index by a quality index and dividing the result by 100. The quantity index and the quality index shall be determined as hereinafter provided.

(a) The basis grade of cottonseed shall be grade 100.

(b) High grades of cottonseed shall be those grades above 100.

(c) Low grades of cottonseed shall be those grades below 100.

§ 28.402 *Determination of quantity index.* The following formulæ shall be used in determining the quantity index of cottonseed:

(a) For cottonseed that by analysis contain 16.5 per cent or more of oil, the quantity index shall equal 4 times the percentage of oil, plus 6 times the percentage of ammonia, plus 5.

(b) For cottonseed that by analysis contain less than 16.5 per cent of oil, the quantity index shall equal 6 times the percentage of oil, plus 6 times the percentage of ammonia, minus 28.

§ 28.403 *Determination of quality index.* The quality index of cottonseed shall be an index of purity and soundness, and shall be determined as follows:

(a) *Prime quality cottonseed.* Cottonseed that by analysis contain not more than 1.0 per cent of foreign matter, not more than 12.0 per cent of moisture, and not more than 1.8 per cent of free fatty acids in the oil in the seed, shall be known as prime quality cottonseed and shall have a quality index of 100.

(b) *Below prime quality cottonseed.* The quality index of cottonseed that, by analysis, contain foreign matter, moisture, or free fatty acids in the oil in the seed, in excess of the percentages prescribed in § 28.403 (a) shall be found by reducing the quality index of prime quality cottonseed as follows:

(1) Four-tenths of a unit for each 0.1 per cent of free fatty acids in the oil in the seed in excess of 1.8 per cent.

(2) One-tenth of a unit for each 0.1 per cent of foreign matter in excess of 1.0 per cent.

(3) One-tenth of a unit for each 0.1 per cent of moisture in excess of 12.0 per cent.

[36] U. S. Department of Agriculture, "Revised Standards for Grades of Cottonseed Sold or Offered for Sale for Crushing Purposes Within the United States, as Amended June 4, 1945," *Federal Register,* **10,** 6640 (June 6, 1945).

(c) *Off quality cottonseed.* Cottonseed that have been treated by either mechanical or chemical process other than the usual cleaning, drying, and ginning (except sterilization required by the United States Department of Agriculture for quarantine purposes), or that are fermented or hot, or that upon analysis are found to contain 12.5 per cent or more of free fatty acids in the oil in the seed, or more than 10.0 per cent of foreign matter, or more than 20.0 per cent of moisture, or more than 25.0 per cent of moisture and foreign matter combined, shall be designated as "off quality cottonseed."

(d) *Below grade cottonseed.* Cottonseed the grade of which when calculated according to § 28.401 is below grade 40.0 shall be designated as "below grade cottonseed," and a numerical grade shall not be indicated.

§ 28.404 *Sampling, analysis, and certification of samples and grades.* The drawing, preparation, and certification of samples of cottonseed, and the analysis and certification of grades of cottonseed shall be performed in accordance with methods approved from time to time for the purposes by the Director of Marketing Services, War Food Administration, or his representatives.

IV. Cottonseed Grade Standards in Use

United States Standards for the grading of cottonseed are what are known as permissive standards in that their use is permissable but not mandatory. Nevertheless, a number of the more progressive of the managers of the cottonseed crushing mills immediately endeavored to apply them in their business. Many difficulties arose. Old theories relative to the composition of cottonseed and old competitive practices arose to plague them. It had long been supposed by many people that all cottonseed ginned at a particular gin or in some storage house, or grown in a particular section of the country were alike. But here was a system of grading which showed great differences in such cottonseed. Adherence to the old theories caused mistrust of the methods of chemical analysis. For many years it had also been the custom in some quarters, when drawing a sample of cottonseed, to grab an occasional handful from the top of a pile or from the seed while it was being loaded or unloaded, in the belief that such samples were representative. But now it was shown that such methods were unreliable. The standards set up a method of sampling, so that all of the different qualities were represented and then commingled and quartered down to a single portion representative of the whole. There were difficulties in teaching the industry the proper technique of drawing, mixing, and quartering samples. Moreover, some mills were inclined to be suspicious of the sampling procedure used by their competitors.

In any market in which a commodity of wide variations in quality is purchased on an "as is" basis, and competition for its purchase is intense, the highest price paid by one competitor, whether based on high quality or on the urge of quantity, soon becomes the general price. The use of a

basis grade and a basis grade price with premiums and discounts for variations in grade was not understood, and so premiums, when paid, were simply added to the basis grade quotation, and so the price was compounded. Since in the past it had not been always admitted that cottonseed varied in value, premiums were thought to be simply a new device of a competitor for paying a high price and thus attract business. The chief obstacle to the full use of the new system of marketing cottonseed appeared to lie in competitive suspicion that some mills might use grading simply as a new and more intricate means of unfair competition.

A. Federal Supervision of Sampling and Grading

It was under the conditions of distrust and uncertainty within the industry, cited above, that beginning with the season of 1937–38 the Department of Agriculture undertook the supervision of the sampling and grading of cottonseed sold for crushing purposes.

Regulations were established [37] providing for the licensing and bonding of samplers, and placing their work under the supervision of agents of the Department of Agriculture. Each applicant for a cottonseed sampler's license was required to have available specified tools for drawing and preparing official samples, and to give a bond in the sum of $1,000 to insure the proper performance of his duties.

Each applicant for a cottonseed chemist's license was required to submit his laboratory equipment for inspection by agents of the Department of Agriculture, to stand a written examination on the principles involved in the chemical analysis of cottonseed, to make an actual demonstration of his ability to determine accurately the quantitative and qualitative composition of cottonseed, and after receiving a license to join each season in the analysis of a series of samples in competition with other chemists engaged in analytical work with cottonseed (see page 550), and finally, under the rating system maintained by the American Oil Chemists' Society, to maintain an annual rating of not less than 90% in analyzing these samples, in order to retain his license.

The regulations further provided that the Department of Agriculture itself would entertain appeals by those having a financial interest in any cottonseed graded by a licensed cottonseed chemist, if the grade certificated by this chemist were disputed or questioned.

B. "As Is" versus Grading Markets

The season of 1937–38 in Mississippi offered a striking contrast between the probabilities of an "as is" market and a market in which cottonseed transactions are based on grading. The entire harvest season was characterized by excessive rainfall. The humidity was so high that cottonseed

[37] *Federal Register*, **3**, 1361–1364 (June 9, 1938).

sprouted in many fields while still in the bolls on the plant. Seed, that was harvested, heated and spoiled so rapidly that every effort was made by the producers and ginners to deliver them to the oil mills as quickly as possible. The seed houses at many of the mills soon became filled with wet seed which heated rapidly and required continuous aeration to prevent their spontaneous combustion. Much of the seed that was received by the oil mills was so high in moisture content that it was impossible to dry them sufficiently for crushing, with the result that to prevent fires and complete spoilage large quantities were removed from storage and dumped in fields to rot.

Under such circumstances, on an "as is" market, it would have been impossible for the mills to continue to operate without concertedly fixing a price based on an anticipated average quality with a fair margin of safety. But, fortunately, cottonseed were being marketed on the basis of grade and the price quoted was for basis grade seed with discounts for low grades consistent with the actual quality of deliveries. The lowest grade acceptable on a gradable basis was grade 25. Seed delivered to the mills from regular customers that graded below 25 were received at a nominal price and either returned to the producers for fertilizer purposes or piled in the open to rot and then given to producers for fertilizer.

At the end of the season it was found that the actual average of the grades sold were as follows[38]: 667 shipments delivered during August averaged in grade 95.9; in September, 8,398 shipments averaged 96.6; in October, 8,405 shipments averaged 100.4; in November, 5,422 shipments averaged 94.3; the average grade of 4,285 December shipments was 85.5; the January deliveries amounted to 2,959 shipments and the average grade was 76.9; in February, 2,600 shipments averaged 72.3 in grade. The entire season based on 36,445 shipments gave an average grade of 91.8. During each month, beginning in November, below-grade shipments were made; a total of 1,511 shipments that graded less than grade 25 were delivered to the oil mills.

Notwithstanding the general prevalence of unfavorable conditions which caused widespread spoilage, there were of course exceptions; of the total lots that were graded, some 12,188 shipments received premiums ranging as high as 17% of the basis grade price, and 22,040 shipments graded above the average grade of the season. Because of the availability of a grading system, producers of these seed received the relatively high price to which they were entitled.

The benefits of marketing cottonseed on the basis of grade accrue to the producer and sellers of seed, and also, to the crushing mills. For the

[38] G. S. Meloy, *Variations in the Composition and Grade of Cottonseed Produced in the States of Arkansas, Louisiana, Mississippi, and Tennessee, Seasons of 1934–35 to 1937–38,* Mimeographed Circular, U.S. Dept. Agr., June, 1939.

producers and sellers of cottonseed, grading makes possible a quotation system based on definite quantities of products for comparison with the current market values of those products. Premium grades should encourage proper care in harvesting and handling, as well as planting and cultural methods which tend to increase the elaboration of oil and protein in cottonseed.

Accurate sampling and grading enable the mills to pay the actual value of the seed received by them. The analyses can be used as a check against mill operation. For instance, the oil yields as indicated by the analyses should be obtained by efficient operation with a variation, plus or minus, of less than two pounds per ton of seed processed. Proper blending of seed of different quality indices should result in material reductions in the discounts for off oil. The danger of excessive losses of oil resulting from mixing extremely low-oil-content seed with seed of high-oil content may be prevented by a study of the grade reports.[32]

V. Incidental Benefits of a Rational Grading System

A. Standards of Mill Efficiency

In the present stage of development of the operation of processing cottonseed, it is not possible to recover either all of the oil or all of the protein. Both oil and protein are lost in the hulls and, in addition, it is mechanically and economically impossible to express all of the oil from the cake.

At the annual convention of the Crushers' Association held in May, 1929, the author suggested that a standard of mill efficiency was essential not only to improve the general average of efficiency of mill operation, and thus raise the average value of cottonseed, but also as a *sine qua non* for the establishment and utilization of any system of grading cottonseed. The subject had been debated in the industry for several seasons, but without any definite result.

The development of a standard of milling efficiency involved consideration of two factors. The first was related to the recovery of protein on the basis of the whole seed. Approximately 2.5% of the protein is located in the hulls and not in the meats. Also, even in the most careful separation of meats and hulls, some meats remain in the hulls. After careful tests, it was found that under good milling practice 92.0% of the total protein should be recovered in the cake, and that the loss of oil should not exceed 60 pounds per ton of seed. The second factor was the efficiency of oil recovery. Since it is mechanically impossible to completely prevent loss of oil during hulling, and since it is not mechanically or economically possible to recover all of the oil from the meats, it was necessary to determine the quantity of oil that would remain in the cake after proper

pressing, together with the loss of oil in the hulls. Although the loss of oil in the hulls varies, it is not now considered good milling practice if more than 4 pounds of oil per ton of seed is lost by absorption in the hulls. This loss is now assumed for practical purposes to be a constant.

The quantity of oil left in the cake is influenced by the manner of preparing the meats for pressing, the pressure applied, the rate of application of pressure, the drainage time allowed, the condition of the press boxes, and the quantity and quality of the resulting cake. With other factors equal, the pounds of oil remaining in the cake of course increases with the quantity of cake recovered per ton of seed; however, at the same time, the efficiency of expressing is increased, so that in terms of percentages the greater the out-turn of cake per ton of seed of any particular protein content, the lower is the percentage of oil in the cake.

At the convention held in May, 1931, a standard of press-room efficiency was adopted. That the establishment of such a standard has been followed by an increase in the general average value of cottonseed as well as in the average efficiency of operation of all mills, may be seen from an examination of the reports of the Bureau of Census. These reports show that for the 10-year period previous to the establishment of the standard of press-room efficiency, the average oil recovery was 306 pounds per ton of seed processed, and that during the succeeding 13 years for which data are available, the recovery of oil has averaged 313 pounds per ton of seed.

The proposed standard after one season's experience was amended; as eventually adopted, it first assumed that at least 94% of the protein should be recovered in the cake. A scale of losses of oil was then set up correlated with the protein content of the seed, and therefore with the quantity and quality of the cake to be produced. The scale of permissible losses of oil based on the production of cake of 41.13% protein content varied from 50 pounds in seed containing 2.80% ammonia (14.38% protein), to 65 pounds for seed containing 4.80% ammonia (24.69% protein). After working under the present standard of efficiency over a period of years, the efficiency of the mills is now such that the author suggested at the convention held in 1943 that the industry was ready, in his opinion, to raise its standard by increasing the assumed protein recovery to 95% and reducing the permissive losses of oil by several pounds over the entire schedule.

B. Market Reports

As a corollary to the supervision of the sampling and grading of cottonseed, the Department of Agriculture undertook to issue a market news report for the benefit of the producers, and ginners of cottonseed, and other middlemen, which would also better inform the crushers of variations in

the quality of cottonseed produced in every section of the Cotton Belt. In order to secure the necessary data for such a market news service, each licensed cottonseed sampler was required to furnish the name of the county and state in which each lot of seed sampled by him was grown or ginned, and each licensed cottonseed chemist was required to furnish the Department of Agriculture promptly with a copy of each grade certificate issued by him. Price information was collected from producers, ginners, merchants, and from cottonseed crushers.

These data were tabulated each week in a report giving the quotations for basis grade seed, the so-called wagon or gin seed prices, the range and average of the grades sold each week, and other pertinent market news. The several items were shown by states and counties of production. Thus for the first time in the history of the cottonseed crushing industry, the raw material consumed by it was placed on an equal footing as to grade and market facilities with corn, wheat, and other farm products.

The marketing of cottonseed on the basis of the standards is now quite general, even though the use of standards is still optional. For several years past, more than 150,000 samples have annually been drawn by licensed samplers, and analyzed and graded by licensed chemists. During the season of 1944–45, nearly 162,000 samples were handled and graded; it is estimated that these samples represented approximately 3,900,000 tons of cottonseed.

C. Accumulation of Statistical Data

Cottonseed grade certificates issued by licensed chemists contain, in addition to the complete analysis of the seed, the name of the county in which the seed were grown or the address of the gin in which ginning was done, the date of the delivery of the seed at the oil mill—and since there is usually only a short delay between the ginning and the delivery of the seed to the oil mills—the approximate date of the harvest. These certificates, therefore, furnish a great mass of statistical data, from which can be deducted the probable causes of the variations in the elaboration of oil and protein, as well as of deterioration of these constituents. Some of these data have already been compiled and reports published.[39]

[39] G. S. Meloy, "Proceedings 48th Annual Convention of the National Cottonseed Products Association, May 17–18, 1944." *Cotton and Cotton Oil Press,* Special Issue, 1944, pp. 43–44.

CHAPTER XI

GRADING AND EVALUATION OF COTTONSEED OIL, CAKE, AND MEAL*

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I. Introduction

The Trading Rules of the National Cottonseed Products Association, formerly the Interstate Cotton Seed Crushers' Association,[1] govern transactions in cottonseed oil, cake, meal, hulls, and linters. For the more valuable products: crude and refined oil, cake, and meal, the Association, through its Rules Committee, has adopted and promulgated standard definitions and permissible variations. Through its Chemists' Committee, in conjunction with various committees of the American Oil Chemists' Society,[2] official methods of analysis have been developed and incorporated in the Rules. These methods must be used by all official chemists of the Association. The development of both trading rules and chemical methods has been an evolution requiring the best thought and study of workers in the industry and technical committees over a period of many years.

The Rules Committee meets jointly with the Chemists' Committee, as provided under the by-laws, for an annual seriatim review of the rules and chemical methods. Only such amendments are made as may be indicated by changed or improved conditions. The policy of the Rules Committee, composed of buyers and sellers, refiners and crude oil manufacturers, brokers and dealers, has been to establish practical standards, and to develop a system of rules and settlements that would be fair to all

* The invaluable assistance of Mr. J. R. Mays, Jr., in the preparation of this chapter is gratefully acknowledged.

[1] The Interstate Cotton Seed Crushers' Association was organized in Nashville, Tennessee, in 1897. In 1929, it was incorporated as the National Cottonseed Products Association at New Orleans, Louisiana. For clarity and brevity, the latter title will be used throughout, or simply abbreviated to Association.

[2] The Society of Cotton Products Analysts was organized in Little Rock, Arkansas, in 1910. In 1920, it was incorporated as the American Oil Chemists' Society at New Orleans, Louisiana. For clarity and brevity, the latter title will be used throughout, or simply abbreviated to Society.

parties concerned. Few changes are now made in established rules or chemical methods, and no changes are made unless the weight of evidence indicates an improvement thereby. All proposed changes in methods of analysis must have the approval of the Chemists' Committee before being referred to the Rules Committee.

The cottonseed industry experienced a rapid growth during the period 1880–1900. Confronted with many problems, its leaders felt the necessity of closer association to develop satisfactory trading procedures and to enlarge the markets for cottonseed products. One of the first steps, after forming an Association, was to create a Rules Committee to establish standards and grades and to regulate transactions in cottonseed products. These early standards were primitive in the light of present definitions and chemical methods. Nevertheless, they were intended to establish a medium for trading between buyer and seller. Indefiniteness and a lack of technical methods made some of these early rules very nearly meaningless. For instance, prime crude oil was required to produce "prime summer yellow grade by the usual refining methods, with a normal loss of weight." Only a few of the large companies operating refineries knew the "usual refining methods" or what was [3] a "normal loss." There were no exact specifications for Prime Summer Yellow Refined oil. Other standards were equally vague and chemical methods were lacking, which led to frequent disputes between buyers and sellers.

The necessity of improving this chaotic condition was recognized by the Association which, in 1903, appointed a committee of three chemists: David Wesson, of The Southern Cotton Oil Company; James Boyce, of The American Cotton Oil Company; and R. B. Hulme, of the Kentucky Refining Company, whose function [4] was to "from time to time give any arbitration chemist pointers on how to refine oil to get the best results." This committee of refiners' chemists continued to function until 1909 when the constitution of the Association was amended to provide for the appointment of a Chemists' Committee, representing more broadly the different interests in the industry. This committee, composed of five members,[5] is charged with the responsibility of recommending methods of analysis to be used by all official chemists of the Association. The first methods, published in 1911,[6] consisted of two pages of vague and indefinite instructions for testing different products. The present section on chemical methods is expanded to cover approximately fifty pages of the Rule Book,[7] and is the

[3] C. B. Cluff, *Oil & Soap,* **22,** Appendix, pp. 13–17 (1945).

[4] National Cottonseed Products Association, *Rules, 1903–04,* p. 9.

[5] The five members represent different branches of the industry, three of its members being referee chemists, one each from the Mississippi Valley, Southeast, and Southwest, and two refiners' chemists, one representing the packing industry.

[6] Interstate Cotton Seed Crushers' Association, Proc. 15th Annual Convention, New York, 1911, pp. 64–66.

[7] National Cottonseed Products Association, *Rules, 1945–46,* pp. 116–164.

result of many years of research and cooperative work conducted by technical committees of the American Oil Chemists' Society.

While the Association has always recognized the excellent work of the American Oil Chemists' Society, it has felt that it was necessary to have its own Chemists' Committee to scrutinize all methods and proposed changes before recommending them for adoption. Consideration of the important relationship of chemical methods to the standards and grades emphasizes the importance of this provision. Some of the more important changes and recommendations of this committee, affecting the development and improvement of methods, will be referred to later in discussing methods of analysis for various products.

The methods of the Association conform to the *Official and Tentative Methods* of the Society (A.O.C.S.) with some few minor variations. Changes proposed by the Uniform Methods Committee of the Society are thoroughly and carefully considered. If approved, the recommendation is submitted to the Rules Committee with an explanation of the effect, if any, upon standard definition or grade of products. The recommendations of the Chemists' Committee have invariably represented the unanimous opinion of its members, and its recommendations are usually adopted without change by the Rules Committee. This evidence of confidence in the Chemists' Committee is in part due to the fact that its personnel has undergone very few changes over the years and its members thoroughly understand the relationship of the rules to the trade.

II. Crude Cottonseed Oil

A. Definition of Grades and Quality

Crude cottonseed oil is traded under the rules of the Association on the basis of certain factors defined [8] under the heading "Definition of Grades and Quality." Under these definitions, flavor and odor, color, and refining loss are the determining factors. Five distinct grades of hydraulic crude oil are established, namely, "Prime," "Basis Prime," "Off," "Reddish Off," and "Low Grade." In addition, definitions also cover "Expeller" and "Slow-Breaking" types. For certain of the grades, limits of refining loss, color, odor, and flavor are established. In actual practice the bulk of oil trading is on "Basis Prime" quality, which covers a very wide range of tenderable oils and which is tied in with the settlement rule covering permissible variations.[9] Only occasionally is crude oil sold under the classification of "Prime." The reason for this is the implied guarantee of quality and the hazards of rejection as contrasted with the liberal provisions of "Basis Prime." In abnormal seasons, when cottonseed have become dam-

[8] National Cottonseed Products Association, *Rules, 1945–46,* p. 58.
[9] National Cottonseed Products Association, *Rules, 1945–46,* p. 75.

aged by weather conditions or through heating in storage, thereby producing low-quality crude, occasional sales are made under one of the three "Off" quality definitions. Except when "Low Grade" crude oil is sold on sample, "Off" quality crudes are subject to the same rules for settlement as is "Basis Prime."

B. Flavor and Odor

Flavor and odor are indefinite qualities, usually regarded collectively. The measurement of flavor and odor is dependent on personal judgment. In more recent years, certain limits of free fatty acids have been established to control the matter of personal judgment on the flavor of crude oils. As a result, chemists rely to a large extent on these limits in determining flavor and odor. Odor, particularly, has entered into the classification of crude oils but to a very limited extent. Under present rules, only two designations of flavor are permissible, namely, "prime" and "off."

The earliest trading rules carried the designation "sweet in odor and flavor" in the definition of prime oils. The word "sweet," clearly a misnomer, was often the subject of discussion in the trade until the adoption of more definite limitations for off flavor, when the word came to be interpreted in its negative sense meaning "not rancid, musty, sour, or bitter." The word "prime" was substituted for "sweet" in 1939 [10] after more than forty years of usage. Where the word "sweet" continues in the definitions describing grades of refined oil, an appended note appears in the Chemists' Section of the Rules [11] interpreting "sweet in flavor" as the "natural flavor of refined cottonseed oil . . . produced from sound seed . . . and free from contamination other than a faint earthy flavor. It shall be expressed as an opinion only."

In the first utilization of free fatty acid limits as a factor in determining flavor, it was attempted to differentiate between slightly off and off flavor by setting a limit of 2.5% for the former and 4.0% for the latter. This developed complications, since there were only two flavor classifications in refined oil—prime and off. In 1941 [12] this rule was changed to designate two classifications, with a free fatty acid content of 3.25% as the dividing point. While it is true that most crude oils with 3.25% free fatty acids possess a slightly off flavor, with the improvement in refining and deodorizing processes it was agreed that allowances for slightly off flavor could be eliminated.

The natural odor of crude cottonseed oil, pressed from sound, prime cottonseed, is pleasant and agreeable. Flavors designated as "off" originate from several sources, as follows: "rancid" is an indication of oxidative

[10] National Cottonseed Products Association, *Rules, 1939–40,* Rule 50, p. 64.
[11] National Cottonseed Products Association, *Rules, 1945–46,* p. 159.
[12] National Cottonseed Products Association, *Rules, 1941–42,* p. 81.

changes and the formation of peroxides; "musty" is usually typical of seed which have undergone field damage or heating; "sour" is a term usually associated with enzymic fermentation occurring in the presence of excessive moisture; and "bitter" is a flavor derived from immature or bollie cottonseed, probably due to tannin absorbed from the hull or boll.

C. Development of a Settlement Basis

The end use of crude cottonseed oil is in the manufacture of such products as shortening, oleomargarine, and salad and cooking oils. Practically all refined oil is used in this manner and only the lowest grades and refining residues enter into nonedible products. The first stage of processing cottonseed oil for its ultimate utilization as a food product is refining with caustic soda. Although chemical methods have been developed [13] for the determination of neutral oil in crude cottonseed oil, it is noteworthy that common practice has prevailed over the years to evaluate crude oil on the basis of a refining test with the use of caustic soda. Such a procedure parallels the process used in commercial practice and has been regarded as a satisfactory indication of the yield of refined oil in actual plant operations.

Less than fifty years ago, during the early days of the Association, when refinery operations were shrouded in secrecy, it was almost considered a disclosure of confidential trade secrets to mention caustic soda in connection with oil refining, hence the earliest rules specified the "usual refining methods." It was not until 1911 [6] that the first methods were published prescribing caustic soda as the refining medium.

In 1901 [14] Prime Crude oil was required to produce a Prime Summer Yellow Refined oil with a color not greater than 35 yellow and 7.1 red on the Lovibond color scale, with a refining loss not exceeding 9.0%. These limits prevailed until 1919, when the color limits were raised to 35 yellow and 7.6 red. Although there have been repeated efforts to lower the basis for refining loss, it has remained unchanged at 9.0%. The laboratory procedure prescribed in the "Chemists' Methods" was designed to approximate factory refining processes and, since experience over many years indicated that 9.0% refining loss was the approximate dividing line between prime and off crude oils, this limit has prevailed.

In more recent years, with the advent and adoption of continuous refining methods in most of the large refineries, the agitation for a change of basis was vigorously renewed. The continuous refining method effects a separation of oil and soapstock, after treatment with caustic soda, by means of centrifuges. The actual contact of oil and the alkali is greatly reduced in the treatment and, by means of centrifuges, a very efficient

[13] D. Wesson, *Oil & Fat Ind.*, **3**, 297–305 (1926).
[14] National Cottonseed Products Association, *Rules, 1901–02*, p. 7.

separation is obtained. The introduction of the first continuous processes for cottonseed oil refining was accompanied by the manufacturers' guarantee of a saving in refining loss over the long-established kettle batch method of refining.

In 1939, the Rules Committee appointed a special committee of crude oil manufacturers, refiners, and chemists to investigate the net saving in continuous refining results over laboratory tests in the case of all grades of oil and to determine an equitable differential, if any, to be used for settlement purposes. This committee reported later that the result of this investigation did not indicate the necessity for an adjustment. Furthermore, no satisfactory laboratory method has been developed for determining refining loss by the procedure used in continuous refining and centrifuging.

D. Crude Oil Settlements

Since the bulk of crude oil is bought and sold on a Basis Prime classification, the buyer is primarily interested in the yield of refined oil. Having a uniform basis for refining loss, color, and flavor, with adjustments for premiums and discounts covering a wide range, enables the buyer to adjust the purchase price on an average yield and quality. Changes in the standards or limits, changes in seasonal quality of crude oil, and economies effected in processing are all factors reflected in the basis price offered by buyers in a highly competitive industry.

Under the settlement rules, premiums are allowed for better than the basis limits on refining loss, with discounts for excess loss and color as measured by these limits. For a period of several years, premiums were allowed on color lighter than 35 yellow and 7.6 red on the Lovibond scale. These premiums were discontinued after it was shown that the buyer derived little benefit from the lighter colored refined oils.[15] The average refined oil derived from prime crude oil, having a color of 35 yellow and 7.6 red, will yield a bleached oil having a color of 20 yellow and 2.5 red, which is the standard color for Bleachable Prime Summer Yellow cottonseed oil. Except for special uses, the limits for Bleachable Refined oil are quite acceptable. Lighter bleached color might be obtained by further processing; however, the additional cost involved would obviate any premium for lighter color which might be obtained.

The earliest trading rules did not carry premiums for better quality but did cover discount and rejection provisions for off quality. The premise that "a tender of a grade of any commodity traded in under these Rules, better than grade sold, will constitute a good tender" has prevailed since early procedures.[16] This provision was intended not so much as a "seller beware" caution as it indicated a lack of adequate procedures and methods

[15] R. H. Fash, *Cotton Oil Press,* **16,** No. 5, 11–12 (1932).
[16] National Cottonseed Products Association, *Rules, 1898,* p. 13.

for arriving at equitable premiums and allowances for superior quality. Correction of these inequalities has found constant expression in actions of the Rules Committee in recommending premiums for better than basis quality where justification for such premiums was indicated.

The early rules provided for discounts of an equivalent percentage of the contract price for loss in excess of 9.0%. This was amended to allow credit for the value of the excess soapstock and, subsequently, was changed to include a charge for the extra cost of handling the excess soapstock. Oils darker than 35 yellow and 7.1 red were at first rejectable. Off oils were usually sold on sample with a permissible variation of 5.0% loss, and an allowance for excess loss. In 1919, Basis Prime Crude oil was defined as crude producing refined oil not darker than 35 yellow and 16.0 red, with a refining loss not exceeding 12.0%, thus extending the limits for crude oil tenderable under this grade. Prior to that time, it was required that Prime Crude produce Prime Summer Yellow Refined oil with provision for allowances for excess loss above 9.0%.

Rule 142, Crude Oil Settlements, was first proposed by a special committee of refiners and crude oil producers meeting in Asheville, North Carolina, in 1926. The amendment suggested by this Committee did not prove satisfactory to the buyers on grounds of its impracticability. A series of three special contracts [17] designated by special code terms, "Factor," "Fabric," and "Fable," were proposed as emergency substitutes as a basis of transactions in crude oil during the season of 1926–27. Subsequently, in 1927, *Rule 142* was rewritten, embodying some of the desirable features included in the special code terms which served as a temporary expedient. For the first time, the principle of premiums, as well as discounts, was given full recognition in the trading rules. Realistically, the provisions for allowances swung too far in the opposite direction, necessitating modification. Subsequently, the rule was rewritten to incorporate these changes, as follows:

Premiums for color lighter than prime were eliminated entirely. Premiums and allowances for losses under or above 9.0% were changed, from 1% of the contract price for each 1% loss, to ¾ of 1%, calculated on the weight of the crude oil. Allowances for slightly off flavor were eliminated, and the provision for an allowance of 1½% of the contract price for off flavor and odor remained unchanged. Later amendments provided that allowances for color, odor, and flavor were to be calculated on the weight of the refined oil produced;

[(100 — per cent refining loss)/100] [weight of crude oil]

all calculations to be figured fractionally throughout. On the basis of these evolutionary changes, transactions between buyer and seller progressed to

[17] *Cotton Oil Press,* **10,** No. 5, 23–24 (1926).

the point of general satisfaction with a minimum of disputes and almost complete elimination of arbitration.

E. Development of the Refining Loss Method

In addition to the above changes in definitions and settlement procedure, a vitally important contribution to improved relations has been the development of an accurate and reproducible laboratory method for determining losses in caustic refining.[18]

The indefinite instructions outlined in the first published methods permitted wide latitude and the exercise of discretion on the part of the chemist in determining refining losses. Any strength of caustic soda, in amount the equivalent of 10% of 16° Bé., was permitted. No definite time limits or speed of agitation were indicated. No temperature of the cooling water was specified. No entrained oil was recovered from the soapstock. In the early methods, no procedure for refining off oils was given.

Shortly after the appointment of the first Chemists' Committee in 1909, the Society of Cotton Products Analysts was organized. Members of this Committee became active workers on the technical committees of the Society, one of which, a Refining Committee, was appointed in 1916 and has continued as one of the important committees of the Society. For a number of years, in the beginning, the personnel of the Uniform Methods Committee and the Chemists' Committee was identical. For a period of about ten years, these committees worked to improve the refining methods by engaging in a large volume of cooperative work. A number of important improvements were made in the method; however, the need for more complete standardization was constantly apparent.

As a result of continuous effort by the Chemists' Committee and later the Refining Committee, many changes and improvements were made in the refining method, in order to cover a wider range of crude oils encountered and also to correct defects found in the procedure.

Specific temperatures and time limits were introduced to control the addition of caustic soda and the time of stirring. Provision for increasing the amount of caustic soda (calculated as dry sodium hydroxide) above the limit of 1.097% was made in order to produce a prime color where the loss did not exceed 9.0%. The first caustic soda tables for use in refining off oil were adopted in 1919. These tables, covering a range of 3.0 to 20.0% free fatty acids, were based on accelerated excesses of caustic soda above the base of 1.097% for oils falling into successive brackets of 2.0% free fatty acids each. The use of these tables was not mandatory and only

[18] C. B. Cluff was a member of the Chemists' Committee for 29 years, continuously from 1915 to 1944. Shortly before his death in 1945, he prepared an interesting history of the Committee, including a brief outline of some of the more important changes in the laboratory refining method. This history was published in *Oil & Soap,* **22,** Appendix, pp. 13–17 (1945).

served as a limit on the amount of caustic soda which could be used for the specified free fatty acid.[19] A very wide latitude was permitted in the selection of caustic soda and in the exercise of judgment on the part of the analyst in many other important factors affecting the final results.

While there were many improvements in refining loss methods, there remained many variables which permitted exercise of discretion and produced results that lacked concordance between different laboratories. These principal variables were: size and shape of the paddles; speed of agitation; temperature, both cold and hot; and amount and strength of lye used for different percentages of free fatty acids. The effect of these variables was not definitely known; also, a method of studying the effect of each variable through cooperative committee work did not seem practical. In 1926, the Chemists' Committee requested the Refining Committee of the American Oil Chemists' Society, of which C. B. Cluff was chairman, to undertake the investigation. It was decided to employ a competent chemist, but one having no preconceived ideas or bias toward the method. The National Cottonseed Products Association appropriated a sum to defray the cost of the work which was placed under the supervision of Cluff and performed in the laboratory of Procter & Gamble Company.

No single contribution to the technical method has done more than this study to clear up discrepancies in laboratory results and eliminate disputes between buyer and seller. It has enabled chemists working on identical samples to arrive at closely agreeing results, thereby eliminating much criticism of laboratories and chemists. Furthermore, results obtained closely approximated results secured in the refinery by the batch refining kettle method.

The various details of the method outlined by Cluff [20] for investigation included the following: size and shape of paddles, size and shape of refining vessel, rate of agitation in the cold, time of agitation (cold), temperature of agitation (cold), rate of agitation (hot), temperature of agitation (hot), rate of heating, temperature of settling, time of settling (hot), temperature of cooling foots, angle of dish during draining of oil, time of draining oil from foots, effect of air bubbles in crude oil, remelting of foots, strength of the caustic soda, effect of different percentages of lye, and impurities in the lye.

All of these variables were studied on two distinct types of oil with two or more tests on each of the principal factors. From a summary of conclusions based on the optimum results obtained in these tests, a proposed revision of the refining loss method was submitted to members of the Refining Committee who, in turn, applied the new procedure to check

[19] National Cottonseed Products Association, *Rules, 1918–19*, p. 56.
[20] C. B. Cluff, *Oil & Fat Ind.*, **3**, 376–381 (1926).

samples sent out by the chairman. The summary of this cooperative work indicated that a recommendation for the adoption of the method was justified. It was adopted and incorporated in the Rules in May, 1927, and with one important exception, has continued to be used unchanged and uninterruptedly since that date.

As indicated by the work of Cluff, variable speed of agitation was found undesirable. Standardization of the refining procedure suggested the necessity of eliminating all possible variables. Fixed speeds of agitation, both in the preliminary cold treatment and the subsequent treatment at elevated temperature, were found to be essential in obtaining more concordant results. The positive control of other variable factors was shown to be necessary.

Prior to this time, several different types of refining machines had been in use, each designed to fit the requirements and personal preferences of the individual user. Of these, the one most generally in use had been designed in 1915 and was equipped with a friction drive which permitted a wide range of speeds of the refining paddles. Following the adoption of the new refining method, an entirely new type of machine with two fixed speeds of agitation became necessary. At the request of the Refining Committee, the designing of such a machine was undertaken and completed during the summer of 1927.[21]

Concurrently, standardization of the refining loss method and the adoption of a refining machine built to rigid specifications have eliminated many of the earlier difficulties. In the hands of a competent analyst, the method is capable of a high degree of accuracy and reproducibility.

In 1928, the method was modified to cover a type of crude oil produced in west Texas and sections of Oklahoma, commonly referred to as the "slow-breaking type." This modification extended the time of cold agitation for such oil from 15 to 45 minutes, and the time for hot agitation from 12 to 20 minutes. Subsequent experience proved that the modified procedure gave more satisfactory results on some prime oils from other sections of the Cotton Belt as well. Changes in the Rules permitted the crusher to designate the type of crude oil as either "regular" or "slow-breaking," such designation indicating the refining method to be used. Consequently, a modification intended as an exception has largely become the general rule. Approximately 75% of all prime oils refine to better advantage by the slow-breaking procedure. Normally, crude oils above 4.0% in free fatty acids refine with a lower refining loss by the regular method.

In expeller mills, when the meats are rolled and cooked before pressing,

[21] A description of the new laboratory refining machine was published in *Oil & Fat Ind.* (July, 1927), and a more detailed description was given by A. E. Bailey *et al.*, in *Oil & Soap,* **19,** 97–102 (1942).

the expressed oil sometimes possesses similar characteristics to hydraulic-pressed oils. A provision of the Rules permits the processor to designate this type of crude as regular, slow-breaking, or expeller, and provides for application of the appropriate laboratory method in determining refining loss.

F. Sampling of Crude Oil

A generally recognized corollary in any method of analysis is that an analysis can be no more accurate than the sample. For many years, wide differences in results were frequently encountered on crude cottonseed oil samples drawn at time of shipment and those taken at destination. This situation naturally led to criticism, dissatisfaction, and frequent disputes.

The contributing factors which caused these discrepancies were the presence of meal settlings and moisture due to improper or insufficient settling of the crude oil. Nearly all crude oil, whether from hydraulic or expeller pressing, contains appreciable quantities of these impurities, which ooze out of the presses with the oil. Unfortunately, due to the mucilaginous character of some nonoil constituents of crude oil, the latter does not lend itself readily to filtration, even with the addition of a filter aid. Therefore, the most effective method of removing these impurities is by prolonged settling in storage tanks. The custom of loading from the bottom of storage tanks, still prevailing at some mills, tends to make the benefits of settling ineffective. The disposal of settlings is always a troublesome problem in oil milling and their presence in crude oil shipments appears to be completely unavoidable, although recent improvements in handling crude oil at the mills have resulted in a betterment of this condition. Sellers of crude oil suffer heavy penalties on account of settlings which, due to other factors, increase the losses in excess of the actual amount of settlings present.

In an article published by the author in 1927,[22] attention was called to the exaggerated effect of meal settlings in crude oil shipments and their elimination was urged. Further details regarding the damaging effects of meal settlings in crude oil were obtained in a series of carefully controlled experiments described in an article published in 1927.[23] Over a period of five weeks, the clear, settled samples of crude oil, to which were added weighed quantities of moist cottonseed meal, showed a rapid and progressive increase in free fatty acids, refining loss, and color.

For many years, the rule for sampling tank cars has provided for the use of a trier of 2-inches uniform diameter, which is closed by a tight valve or cock. With the valve open, the trier is lowered to the bottom of

[22] E. R. Barrow, *Oil & Fat Ind.*, **4**, 383–385 (1927).
[23] E. R. Barrow, *Cotton Oil Press*, **11**, No. 7, 21–23 (1927).

the tank; the valve is then closed and the trier withdrawn. After several takes in this manner, the samples are thoroughly mixed and transferred to clean, new 1-gallon containers. Obviously, on perfectly clear oil or on oil in which the suspended matter is evenly distributed by agitation, this method of sampling yields a fair and representative sample. On the other hand, when meal settlings are present, since the tank cars are usually several days in transit, this suspended matter settles out along the bottom, thereby increasing the difficulty of obtaining a representative sample.

Tank cars are cylindrical in shape, having an average diameter of 75 inches. To illustrate the fallacy inherent in the destination sampling of oil containing much settlings, let us assume a ¾-inch layer of settlings on the bottom of the tank; this is equivalent to 1% of the core sample drawn according to the official rules. However, this ¾-inch layer represents approximately only 0.2% of the total cubical contents of the tank. Consequently, by this sampling procedure, the actual amount of settlings present is magnified five times. The situation described here is illustrated in Figure 118.

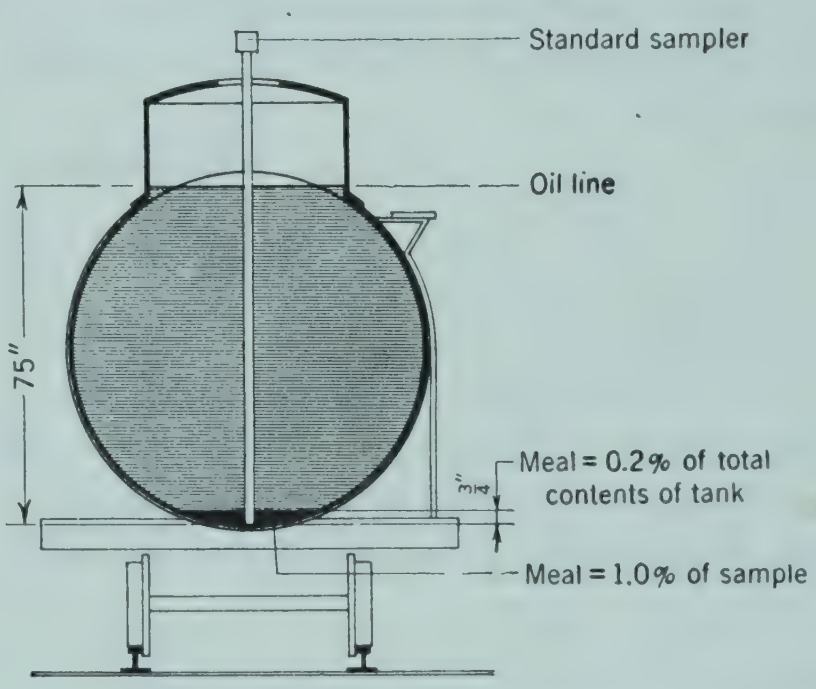


Fig. 118. Graphic representation of the exaggerated effect produced on the official sample by a small percentage of meal in the bottom of a tank car of oil.

In making a laboratory refining of a sample of crude oil containing suspended matter, the settlings act as an emulsifying agent, increasing neutral oil saponification, and carrying down entrained oil to the extent of increasing refining loss by an amount equal to from four to seven times the actual amount of settlings present in the sample. All of these penalties accrue against the seller and, should there be unusual delay in making the settlement analysis, fermentation of the moisture-containing settlings will take place, causing an increase in free fatty acids with a further increase in refining loss and possible effect on both color and flavor.

The cumulative effect of increased penalties due to the presence of settlings engaged the attention of the trade and the Rules Committee. A committee was appointed to study the problem and suggest a remedy. The first suggestion of agitating tanks with air at the destination met with objections as being impractical. An alternate suggestion that official sampling be permitted at the point of origin after the tank is fully loaded

met some objection, due to the fact that crude oil is sold on weight and quality guaranteed at destination, but was finally adopted in 1941 as an alternative to the long-established procedure of using a trier for drawing the sample at the destination.

The Rule provides that the sampling at the point of origin be performed by an official weigher and inspector at interior points. This has necessitated the appointment of deputies by the Association. These deputies represent commercial laboratories whose principals are in themselves appointees of the Association and who are responsible to the Association for the faithful performance of the deputies. A portion of the official sample is immediately sent to the buyer and another portion to an official chemist, thus eliminating the usual delay in settlement analyses. It is required that the point-of-origin official sample reach the buyer prior to unloading of the tank; otherwise, an official destination sample is drawn which governs the settlement for quality.

III. Refined Oil

A. Flavor and Odor

Refined oils are graded on a basis of odor, flavor, and color, with defined limits for free fatty acid and dissolved moisture contents. Odor and flavor, collectively, constitute a matter of personal judgment, dependent on the experience of the analyst. Only two classifications of flavor are designated under the Rules, namely, "prime" and "off."

B. Color

The color of both refined and bleached oil is determined by comparison with red and yellow Lovibond color glasses in a suitable tintometer. Early discovery of inaccuracies existing in the nominal valuations of some of the color glasses led to an intensive study of the whole subject of color comparison, which was conducted by the U.S. Bureau of Standards. The work of I. G. Priest and his associates started about 1913 and continued for a number of years. In his first report, Priest [24] outlined the results of his investigations on the variations existing between the indicated and actual values on many Lovibond glasses, as determined by the Arons Chromoscope, and recommended the substitution of an exact optical instrument for evaluation of color in both refined and bleached oils. Such an instrument would express color readings in terms of absorption at different wave length rather than by Lovibond equivalents.

However, this suggestion was confronted with several obstacles: first, the high cost of modifying or perfecting an optical instrument, and second, the rather fixed acceptance by the trade of color readings expressed in

[24] I. G. Priest, *Cotton Oil Press*, **3**, No. 3, 86–88 (1919).

terms of the Lovibond scale. Attention was turned to the standardization of color glasses and this work continued over a period of years. Within the last few years, the early recommendations of Priest have been revived and give promise of the development of photoelectric methods which will replace the present outmoded procedure, depending as it does too largely on the personal equation. It is probable that the industry would now be in a more receptive mood toward such a change than was the case in its earlier history.

The Chemists' Methods now provide that all red glasses in the standard set specified must be standardized by the Bureau of Standards. Many improvements, likewise, have been made in the color comparator or tintometer. The type now specified is known as the Wesson Enclosed Tintometer. It consists of a lightproof box with dull black interior which is illuminated by a 100-watt, frosted daylight (blue) bulb, with the light being reflected upward from a magnesia block through a tube containing the sample of oil. The standard color glasses, through which the light is also reflected, are held either in a receptacle or in the form of discs embedded in movable concentric rings. An eyepiece fits over the oil tube and color glasses so that the light passing through each may be observed simultaneously. All color readings are made on a column of oil 5¼ inches in depth in a tube of approximately ¾-inch inside diameter.[25]

For the determination of grade, it is only necessary to compare the sample of oil with the standard glasses specified. In the case of refined oil, 35 yellow and 7.6 red, and in the case of bleachable oil, 20 yellow and 2.5 red (after bleaching) constitute the color limits for grade. However, it is customary to report color readings as indicated by exactly matching the oil with the Lovibond glasses.

C. Bleaching Test

The test [26] for bleachability of refined cottonseed oil is made by heating a weighed quantity of oil to a temperature of 120° C., adding 6% of Official Fuller's Earth, stirring at 250 ± 10 r.p.m. for five minutes, and then filtering. A slight modification of the mechanical stirrer previously described is used to supply the agitation. The color readings are made on the cooled filtered oil, using the Wesson-type tintometer.

D. Cold Test

Winterized oils as defined in the Rules are subjected to a cold test to determine the effectiveness of stearine removal. This test consists of submerging a four-ounce sample bottle of oil in a vessel of finely cracked

[25] More detailed information is found in "History of the Color Committee," by G. W. Agee, published in *Oil & Soap,* **22,** No. 12, Appendix, pp. 16–17 (1945).

[26] National Cottonseed Products Association, *Rules, 1945–46,* Rule 275, p. 160.

ice and sufficient water to surround the bottle. After 5½ hours, the sample is examined and must be clear, brilliant, and limpid.

IV. Cottonseed Meal

A. Development of Grade and Quality

The earliest official definitions of cottonseed meal were given in terms of physical characteristics without reference to the most valuable constituent—protein. This omission was shortly remedied. Instead of using the term protein, its ammonia equivalent was the term used in defining the feeding value. Such descriptions as "canary yellow," "reasonably bright," and "yellowish" constituted perhaps the most accurate means of defining a product which had not felt the influence of technical control.

From the beginning, the industry attempted to control adulteration by specifying in its Rules, for meal, that it must be free from "excess hulls and lint." One of the most troublesome problems encountered was the elimination of excess lint, the presence of which was caused by the inadequacy of the delinting machines available at the time. This condition remedied itself as more efficient machines were perfected and as the value of the resultant linters steadily increased. By reason of the very nature of the cottonseed manufacturing process, a complete separation of the hull from the kernel is neither practicable nor desirable. To obtain the highest efficiency in oil extraction, a reasonable amount of hulls is generally considered necessary to effect proper oil drainage. Also, hulls are required for the most economical and efficient regulation and control of protein content, which varies with the composition of the cottonseed. Rigid chemical control in oil mill operations now enables these factors to be regulated.

B. Geographical Characteristics

Still another important factor complicating standardization of meal grades is the variable quality of cottonseed. Aside from the widely fluctuating oil and protein content within localized territories, there exists a rather definite geographical differentiation of these important constituents. In the western States, cottonseed are characterized by high-protein and low-oil content. In the southeastern or Atlantic Seaboard States, the reverse of this condition prevails, whereas, in the Middle or Valley States, a mixture of both conditions is encountered. These geographical characteristics are ascribed to the effects of climate, soil, cultural methods, and variety, which exert a very definite influence on the composition of cottonseed.

Serious objection was raised to the establishment of 8.00% ammonia as the basis for Prime Meal on account of a low-protein content in cottonseed in a large part of the Cotton Belt. To meet this condition, the basis was lowered to 7.50% ammonia for the South Atlantic States, with the

8.00% ammonia basis being continued for the remainder of the Cotton Belt. Such differentiation, however, soon developed trade discrimination, necessitating further amendments.

C. Standard Definitions

The next important change was that of defining the three grades of meal, "Choice," "Prime," and "Off," with the ammonia fixed at 7.50% and 7.00%, respectively, for the two higher grades. Shortly thereafter, these ammonia limits were raised to 8.00% for "Choice," and 7.50% for "Prime," with the addition of 7.00% for "Off." In 1921, the Rules Committee redefined the above grades, eliminating the terms "Choice," "Prime," and "Off," and substituted protein equivalents of the former ammonia bases as the means of designating the grades. This more rational practice of evaluating meal in terms of protein rather than ammonia has continued uninterruptedly. However, the same objection to trade discrimination, based on the terms used to define the three grades, was again encountered, resulting in the establishment of a new definition for Prime Quality Cottonseed Meal with a minimum 36.00% protein guarantee, to be designated "36.00% Protein, Cottonseed Meal, Prime Quality." Higher grades were to be similarly designated on the basis of the protein guaranteed. Very few changes have been made in the definition of Prime Quality Meal in recent years. Prime Quality as now defined in the Rules "must be finely ground, not necessarily bolted, must not have a sour or musty odor, must be free from excess lint, and shall contain not less than 36.00% of protein, 7.00% of ammonia, or 5.76% of nitrogen. It shall be designated and sold according to its protein, its ammonia, or its nitrogen content." [27]

D. Development of Uniform Feed Laws

Cottonseed meal is declared to be "a product of the cottonseed only, principally of the kernel, with such portion of the fiber or hull and oil as may be left in the course of manufacture." This conforms to the definition adopted by the American Feed Control Officials. In the effort to arrive at a definition which would be inclusive and still not disqualifying or discriminatory, there was another difficulty to be met. Nearly all of the states passed feed laws regulating the sale of feeds within their borders. These laws required registration of the feeds offered for sale and set up standards and other requirements. Devised as protective measures, they often contained drastic provisions which inflicted hardships on manufacturers of feedstuffs. Lack of uniformity caused endless confusion. What was an acceptable commodity in one state might be refused registration or fail to meet the standards in another. A demand for uniform feed laws de-

[27] National Cottonseed Products Association, *Rules, 1945–46,* Rules 100 and 101, p. 64.

veloped from manufacturers and trade associations throughout the feed industry.

Fortunately, in January, 1910, the Association of Feed Control Officials was organized in Washington, D. C. This association, composed of national and state officers who administer the feed laws, invited suggestions and information pertaining to the drafting of a uniform feed law. A committee on uniform feed laws was appointed in the same year by the Association [28] and has continued to function by contacts with the Feed Control Officials at their annual meetings. Through an understanding and fair-minded approach to mutual problems, these two groups have performed an outstanding service to the industry and to the public. Fair and equitable standards have been established and have received general recognition by the trade. The lack of uniformity and confusion existing in early feed laws has practically been eliminated. The frequent conferences between committees representing the two associations have developed mutual understanding and cooperation, resulting in the establishment of practical and improved definitions.

V. Cottonseed Cake

A. Development of Grade and Quality

Cottonseed cake is the product remaining after the expression of the oil in the hydraulic process. Since it has a higher density than cottonseed meal, it is frequently shipped as cake without grinding. Particularly in export shipments, this form is preferred. Cake grinding and feed manufacturing plants are buyers of cottonseed cake, which is reduced to meal to be marketed under special brands or used in formulating mixed feeds. Sized cake is used extensively in range feeding, particularly in the West. In recent years, however, the use of cottonseed pellets has replaced to some extent that of sized cake. Pellets are made in special machines in which either cake screenings or meal is subjected to high pressure.

Cottonseed cake is sold on a definite protein content, which may be expressed in its equivalent ammonia or nitrogen percentages. The basis grade is the same as cottonseed meal, namely, 36.00% protein, 7.00% ammonia, or 5.76% nitrogen, with higher grades being designated similarly according to content of protein.

The Rules of the Association [29] define Cottonseed Cake, Prime Quality, as: "firm, but not flinty in texture, must not have a sour or musty odor, must be free of mold and must produce, when ground into meal, Prime Quality Cottonseed Meal. It shall be designated and sold according to its

[28] Interstate Cotton Seed Crushers' Association, Proc. 14th Annual Convention. Little Rock, Arkansas, 1910, p. 106.

[29] National Cottonseed Products Association, *Rules, 1945–46,* Rule 86, pp. 62–63.

protein, its ammonia, or its nitrogen content." Another section of the Rule defines Prime Quality Cake in cube or pellet form, which must conform to the definition of Prime Cake. Five grades of screened, sized cake are defined, with the gradation specified for each grade. In each of these grades, the minimum percentage of protein must be specified, but this is left to the discretion of the manufacturers or the buyers. The changes which have occurred in the ammonia or protein guarantees for cottonseed meal through the evolution of standard grades and quality have had their counterpart in the definitions of cottonseed cake. Whenever changes have occurred in these guarantees, such changes have applied simultaneously to both meal and cake.

B. Whole-Pressed Cottonseed

The introduction of expeller pressing of whole seed in cottonseed manufacture brought about the need of special rules covering the products from this process. The first rule defining the expeller product was adopted in 1914, when it was designated as "cold-pressed cottonseed flake" and carried no protein guarantee. From time to time it has been designated as "Cold-Pressed," "Whole-Pressed," or "Expeller Cake," carrying a protein guarantee of 20.00%. Finally in 1935, the present term, "Whole-Pressed Cottonseed," was adopted. This designation more clearly differentiates between the product made from the whole seed and that produced from decorticated seed and known throughout the trade as cottonseed cake.

It is to be noted that expeller pressing of decorticated cottonseed produces a cake not usually different in protein content from hydraulic pressing.

C. Sampling Cottonseed Cake

One of the most difficult problems in grading cottonseed cake has always been the matter of drawing and preparing correct samples. Even the individual slabs of cake sometimes vary widely in protein content in different portions. The early rules provided for a sample composed of six slabs to represent a carload of twenty tons or more. This was changed to "at least six," allowing the sampler to exercise his option. Frequent differences in chemical analyses were the natural outcome of taking non-representative samples. It was difficult to draw two samples from the same lot which would give like results upon analysis. Chemists were often severely criticized for inconsistencies in their analyses.

After a very extensive study, accompanied by many analyses of samples drawn under varying conditions, it was found that a representative sample could be obtained by increasing the number of units in the sample and then selecting portions according to a mathematical formula.

This study, with the accompanying analytical work, was performed by Barrow-Agee Laboratories, Inc., in their Memphis laboratory. Analytical data had indicated that sometimes wide differences in protein content existed among different samples of the same lot of cake drawn in the manner then prescribed in the Rules. Differences were also found to exist between samples representing individual whole cakes ground into meal. Furthermore, analyses of segments of individual cakes representing corners, middles, ends, sides, and centers disclosed wide variations in protein content.

Confronted with these variables, the problem was to find a practical method of sampling which would overcome or neutralize their effect. An increase in the number of cake slabs represented in each sample was indicated in order to make the sample more representative. However, since the approximate average weight of a slab of cake is 16 pounds, a sample containing a large enough number of whole cakes to be representative would have a prohibitive weight. By applying the analytical data showing the variations in analyses of segments taken from different positions in the individual cake, a diagram was developed for dividing the cake into a number of equal segments and taking a proportionate number of segments to represent the different positions marked on the diagram, namely, corners, centers, ends, middles, and sides. A sample of limited size would then represent a cross section of the total number of cakes sampled.

Many samples were drawn in this manner—prepared and analyzed. The results indicated a very close agreement in analytical results between different samples of the same lot. Each segment taken in accordance with the prescribed method weighed approximately one pound, so that a sample taken from thirty cakes would weigh approximately thirty pounds, a practical size for samples drawn from cars on tracks or at the plant. The large sample, consisting of thirty pieces, was reduced by passing the entire sample through a cake breaker, thoroughly mixing, quartering to the desired size, and then grinding into meal of the desired fineness.

A	*D*	*D*	*D*	*A*
B	*C*	*C*	*C*	*B*
A	*D*	*D*	*D*	*A*

Fig. 119. Sectional diagram showing the method of obtaining proportionate segments of cake to form a representative sample.

The diagram of Figure 119 illustrates the position of the different segments and the method [30] of sampling is as follows:

From the first eight slabs of cake, take the pieces from positions marked *A* on the diagram; from the next four slabs, take a piece from the position designated *B*;

[30] National Cottonseed Products Association, *Rules, 1945–46*, Rule 244, Sec. 1(a), pp. 106–107.

from the next six slabs, from the position designated *C*; and from the next twelve slabs, from the position designated *D*—a total of thirty pieces.

Experience has proven that this method of sampling, when properly performed, results in an accurate and reproducible sample. Its use has eliminated many of the wide differences in analyses of cottonseed cake previously encountered.

Although cottonseed cake and meal are sold on a basis of protein, ammonia, or nitrogen content, both contain another valuable element which does not enter directly into their evaluation as feedstuffs. Hydraulic-pressed cake usually contains at least 4.50% oil; whole-pressed or expeller cake, at least 4.00%. While cottonseed cake and meal are regarded primarily as protein concentrates, this other valuable ingredient undoubtedly enhances their value as cattle feeds and becomes an important factor in supplying the fat element of mixed feeds. In states where uniform feed laws require the registration of brands, the Rules of the Association suggest certain guarantees of protein, fat, fiber, and nitrogen-free extract content for the three grades of cake or meal defined in the Rules.

VI. Methods of Analysis for Cake and Meal

A. Introduction

The difficulties faced in developing methods for evaluating cottonseed oil were not encountered to the same degree in developing methods for cake and meal. The Association of Official Agricultural Chemists came into existence on September 9, 1884. Many able committees of this Association, composed of leading federal and state chemists, were constantly at work studying to develop and improve analytical methods covering a wide variety of products, including grains and agricultural by-products. The published methods of the A.O.A.C were the accepted procedures to be followed in analyzing such commodities. However, in the application of the methods for moisture, oil, and protein, which are the usual determinations required for a meal or cake analysis, certain modifications were soon found to be necessary.

B. Moisture

The moisture determination has never proved to be an accurate or reliable method. It merely records the loss in weight of a given quantity of a sample heated at a specified temperature for a given time. Reasonably concordant results by an individual on portions of an identical sample, using identical equipment, may be obtained. However, between different analysts working on samples alleged to be identical, wide differences frequently exist. The early methods provided that the sample could be

between 2 and 5 g. in weight, and that it should be dried for three hours at a temperature of 100° C. Water-jacketed ovens were the usual type used. Varying with the size of the oven and the water level, the temperature might easily differ by several degrees from that specified. Committees of the American Oil Chemists' Society have been working on this problem for many years and have made some improvement in the method.

Development of the electrically heated, thermostatically controlled, circulatory-type oven has proven to be the greatest advance in standardization of the moisture determination. Under careful regulation of both operation and load, uniform results may be obtained. However, there still exists some question regarding the accuracy of the method, the study of which is now being continued.

C. Oil Determination

1. The Solvent

It was necessary from the beginning to select a different fat solvent from that specified by the A.O.A.C. Anhydrous ethyl ether was found to extract certain nonoil constituents of cottonseed meal, thereby yielding high results. Carbon disulfide was used as a solvent to a limited extent. It is not recorded who first proposed the use of petroleum ether as a solvent for cottonseed oil in extraction work. It was in use in laboratories of some of the large companies prior to 1900. From the beginning, it has been recognized as the most suitable and satisfactory solvent for cottonseed oil.

For many years, prior to the adoption of definite specifications for petroleum ether, its chief source was what was commonly known as "gas machine gasoline." The product is a condensate of casing head gas, formerly a waste product in the petroleum oil fields. Undefined methods of distillation and variable supplies of "gas machine gasoline" resulted in a distillate covering a wide boiling point range.

One of the large petroleum companies, Skelly Oil Company, specializing in fractionating the lighter naphthas for the production of industrial solvents, became interested in developing a solvent to be used for extraction work in vegetable oilseed laboratories, and placed a standardized product on the market. For the first time, the chemical laboratories using petroleum ether could depend on a solvent of definite specifications. These specifications were adopted in 1931.[31] Only minor changes have been made in the original specifications for the purpose of improving the quality of the product. The availability and use of a standard solvent has been a valuable contribution to the accuracy of the oil determination.

[31] National Cottonseed Products Association, *Rules, 1931–32*, Rule 272, Sec. 3, p. 130.

2. Apparatus and Technique

Perhaps the most valuable contribution toward improving the technique and accuracy of the oil determination in cottonseed products was the work of the Extraction Committee under Dr. H. B. Battle, reported in 1919.[32] Prior to the investigations of this Committee, the method [33] specified that the chemist should "extract two to five grams of sample for three hours in any suitable fat extraction apparatus, using petrolic ether, boiling below 65° C., as the solvent." Questionnaires sent to members disclosed a wide exercise of discretion in interpreting these vague directions.

An intensive study of each of the variable factors, involving the analyses of many samples, was made by members of the Committee and other collaborators. As a result of this important research, the method was standardized as to procedure and immediately incorporated in the Rules of the Association. Aside from definite specifications fixing weight of sample and time of extraction, the adoption of the Butt-type extraction tube and a simple method of double-wrapping the sample in filter paper were the two outstanding improvements in the method. The standardization of the extraction procedure has resulted in a very high degree of accuracy and reproducibility. Except for a few minor changes in the method to add to its refinement, the recommendation of this Committee has been used continuously since its adoption.

D. Nitrogen, Ammonia, Protein

Fortunately, the proven methods for determining nitrogen in organic materials, developed by the Association of Official Agricultural Chemists, were available as a basis for similar analytical methods applicable to cottonseed and cottonseed products. Unlike some of the official methods now in use, which fall under the classification of empirical methods, the nitrogen determination is essentially a chemical method depending on definite chemical reactions. The modified Kjeldahl method, as defined by the A.O.A.C., was the original method adopted for analyzing cottonseed cake and meal under the Official Methods of the Association. It is surprising how few changes have occurred in the original method as proposed by the Chemists' Committee and printed in the Rules of the Association for the first time in 1911.[6] This method is designated by the A.O.A.C. as the Kjeldahl-Gunning-Arnold method for nitrogen.

Lack of uniformity and impurity of chemical reagents constituted the major difficulties encountered in the early use of the method. These conditions have vastly improved. The quality of chemical reagents has

[32] H. B. Battle, *Cotton Oil Press,* **3,** No. 3, 91–95 (1919).
[33] National Cottonseed Products Association, *Rules, 1918–19,* p. 53.

attained a high state of purity and can be depended upon for uniformity. Likewise, since World War I, American glassware manufacturers have so improved the quality and efficiency of chemical glassware as to far excel their European predecessors. Preparation and preservation of samples, improved laboratory technique, along with more accurate analytical balances and other apparatus have all exerted an influence in perfecting the accuracy of the nitrogen determination.

E. The Smalley Foundation

Any discussion of chemical methods used in analyzing cottonseed cake or meal would be incomplete without reference to a unique and effective system of cooperative check work, known as the Smalley Foundation. Begun about 1912 by Dr. F. N. Smalley, Chief Chemist of The Southern Cotton Oil Company, as a means of checking the work of that company's laboratories, it was extended to others who asked to participate, as a means of checking the accuracy of their own work. The number of participants now ranges between 80 and 100. The list includes all Official or Referee Chemists, who are required to analyze the series of thirty meal samples. A large number of federal, state, and plant control chemists also take part in the work.

Dr. Smalley died in 1921 and the following year, in recognition of his brilliant career as a chemist, the Society adopted the title "Smalley Foundation" for the system of collaborative work originated and fostered by him.

The work has been invaluable in improving the accuracy of the chemical analysis of cottonseed cake and meal. Participating federal and state chemists have been afforded an opportunity to compare their results with chemists engaged in industry. Using the same methods and analyzing the same samples has resulted in comparisons that have eliminated many differences in results which formerly existed. Improved accuracy, applied to control of production, has developed better compliance with federal and state regulations, as well as a better understanding and more effective enforcement.

Next in importance to the accuracy of the methods is the preparation of accurate samples. This work, performed for many years by T. C. Law of Atlanta, Georgia, has been an invaluable contribution to the success of the Smalley Foundation. Undoubtedly, as a result of the Smalley Foundation, the determinations of oil and nitrogen in cottonseed meal have reached a very high degree of accuracy and precision. The Smalley Foundation, sponsored by the American Oil Chemists' Society, occupies a unique position among technical groups as a means of checking the accuracy of analytical work among laboratories.

VII. Summary

The evolution of the Trading Rules and Chemical Methods of the National Cottonseed Products Association has established a fair and equitable basis of trading between buyers and sellers. The definitions of grade and quality for cottonseed products recognize certain chemical characteristics which are used as a basis for establishing standards. Deviations from these standards of quality, within definite limits, are provided for in settlement rules fixing premiums and discounts for permissible variations. A very intimate relationship exists between chemical methods and definitions of grades and quality. As more accurate chemical methods have been developed, the Rules have become more specific in defining quality and grades. Whereas in the early days there were many disputes and costly arbitrations, due to the inadequacy of both rules and methods, in recent years these controversies are practically nonexistent.

In furtherance of its rules and to provide an equitable basis of settlement for any disputes which might arise, the Association has established a practical, inexpensive system of arbitration and maintains arbitration committees at all of the principal centers trading in cottonseed products. Due to the efficacy of the Rules and Chemical Methods, these committees remain practically inactive. As a consequence of this development, the Trading Rules of the National Cottonseed Products Association are held in high regard and represent a unique example of industry self-control.

CHAPTER XII

GRADING OF COTTON LINTERS

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I. Early History of Linters

Cotton linters were long looked upon as an unwelcome by-product of the United States' cottonseed crushing industry. For many years, the product was classed with wastes and handled chiefly by waste and junk dealers. Under such circumstances the recovery of linters was frequently attended with carelessness and neglect. When done at all, delinting was undertaken primarily to save oil and to facilitate the separation of the meats or kernels from the hulls. To secure the meats, the seeds are cracked or cut and the hulls separated from the meats over beaters and shakers. During this operation, the residual fibers, if not removed, will absorb oil, and during the shaking and sifting are likely to become felted and to enmesh portions of the kernels, which therefore cannot be recovered economically. The absorbed oil in the fiber and hulls and the entrapped meats constituted a serious loss.

As received at the oil mills, cottonseed always contain more or less foreign matter, consisting of sand and dirt, leaves and sticks, stones, and even hardware. For many years, since linters were considered of little value, it was customary to eliminate only such foreign matter as might damage the linter machines, and to permit the residue to pass through and be incorporated with the linters. This, of course, resulted in the inclusion of much trash. As new uses for linters were developed, the demand for this product grew, and the importance of producing linters free from foreign matter became more and more evident. For some years now, increasingly more attention has been given to the thorough cleaning of the seed before delinting and, more recently, to the further cleaning of the linters before baling. Although the delinting of cottonseed was originally undertaken as one of the steps in conditioning the seed for oil extraction, it was soon found that this fiber had in itself an economic value. It became the practice, therefore, to bale the fiber and to offer it

for sale. It was not until the season of 1899–1900 that separate statistics were made available relative to the production of linters. During that season, 53% of the cottonseed produced were processed. About 23 pounds of fiber were recovered per ton of seed, and a total of 114,544 bales, each of 500 pounds net weight, were produced. This fiber brought an average of $3.14 per cwt. The crop produced in the season of 1914–15, however, brought an average of only $1.50 per cwt. The production has increased until now approximately one million bales are produced annually.

II. Factors Influencing Production

There is no consistent relation between the production of cotton and the production of cotton linters. It might be supposed that the greater the production of cotton the greater would be the production of cottonseed, and therefore the higher the production of linters. This supposition neglects the fact that the production of linters is mechanically controllable and that the control is influenced by the market for linters. A low price and a poor demand for linters results in reduced production. Moreover, the portion of the cottonseed produced that is marketed for crushing purposes is influenced by the producer's reaction to the price offered for cottonseed and to some extent by weather and transportation conditions. The irregularity in the ratio of the production of linters to the production of cottonseed is illustrated by a comparison of the production figures for a few seasons as indicated in Table 159.

TABLE 159

Comparative Production of Cotton, Cottonseed, and Linters in Different Seasons[a]

Season	Cotton production, equivalent 500-lb. bales	Cottonseed processed, tons	Estimated percentage of total cottonseed processed	Linters produced, equivalent 500-lb. bales	Ratio cotton to linters	Recovery of linters per ton of seed, lb.
1916–17	11,302,375	4,479,176	87.6	1,330,714	11.8	149
1920–21	13,439,603	4,069,166	68.1	422,226	3.1	54
1926–27	17,977,374	6,305,775	78.9	1,157,861	6.4	92
1937–38	18,415,446	6,325,733	75.0	1,819,219	9.9	144
1942–43	12,819,506	4,497,779	78.6	1,705,856	13.3	190
1943–44	11,428,747	3,954,542	84.5	1,464,510	12.8	185

[a] *U.S. Bureau of the Census* figures.

III. Definition and Nature of Linters

Some uncertainty still seems to exist regarding the nature of the commodity known as linters. The name is derived from the machine used to remove the fiber from the cottonseed. This machine is in fact a modified

cotton gin, which is the machine used to separate the commercial lint cotton from the seed; to distinguish the two machines, one is called a gin and the other a linter. Linters may be said to be composed of the residual fibers found on cottonseed after they have been put through the usual process of ginning.

The seed of all varieties of American upland cotton produce two distinct types of hair. First in point of use and value is the long creamy white hair or fiber generally called lint or cotton, the length of which is a varietal characteristic and ranges from about $\frac{5}{8}$ inch to more than $1\frac{1}{2}$ inches. The second type of hair is a comparatively short fiber generally spoken of as fuzz. Fuzz frequently has considerable color, which is usually olive at first but which upon exposure to light gradually turns to a creamy color and finally to buff. Under the microscope, the fuzz fibers can be distinguished from the long fibers by their comparative smoothness or lack of convolutions, their broadness at the base where attached to the seed, their shortness, and their characteristic of tapering rapidly and regularly to the tip. The long hairs or cotton, by contrast, are generally somewhat convoluted, have a comparatively uniform width for a considerable portion of their length, and end in a relatively long tapering point. In the process of ginning, most of the long hairs are removed from the seed, as is also, more or less, the short hair or fuzz, with the amount removed depending upon the condition of the seed cotton, and the mechanical condition of the gin and the manner of its operation. Some of the long hairs escape through the gin without being detached from the seed. These are usually softer hairs that do not have the wiriness and resiliency usually acquired during the drying out and curing of the fibers after the bolls open. The wiriness and resiliency are manifested by unfolding and fluffing of the more robust fibers, while the flaccid fibers remain matted about the seed. Under the microscope, the latter appear generally more translucent than the robust fibers and in cross section are ribbon-shaped and show very few of the thickened longitudinal ridges that are irregularly distributed throughout the length of most normal cotton fibers. The ridges that are seen are not as pronounced as those of robust fibers. The quantity of these flaccid fibers that escape ginning bears a direct relation to the length of staple of the cotton and an indirect relation to the care with which the ginning operation is carried out. A careful ginner, for instance, will allow the softer unfluffed fibers to pass unginned, since, because of their softness and color, they reduce the grade and value of the cotton. The longer the staple is, the greater is the relative grade value and, therefore, the greater the demand for care in ginning, *i.e.*, for permitting the escape of faulty, matted, or unfluffed fibers.

In the ginning of short staple varieties of cotton, the amount of residual fiber—both long fiber and fuzz—remaining on the seed after ginning

depends upon the sharpness and the speed of the saws, the tightness or hardness of the seed roll in the gin breast, and the moisture content of the seed. The harder the roll and the faster and sharper the saws, the closer the seed are denuded. It is evident that some of both the flaccid fibers and fuzz are regularly taken off the seed in ginning, since card fly is composed very largely of such fiber.

Practically every lot of ginned seed varies from every other lot in the amount and character of the residual fibers. The amount of residual fibers on seed as received by the cottonseed oil mills varies from about 3 to 18% by weight, and averages approximately 10%. The consignments of cottonseed that reach the oil mills, therefore, vary considerably in character. At the mills, the seed are first freed of foreign matter and then reginned or "delinted" on linter machines. Since the linter machine is similar in construction and operation to a saw gin, here again there is variation in the amount of fiber or "linters" removed, depending upon the sharpness and speed of the saws, the hardness of the seed roll, and the rate of escape of the seed from the machines.

IV. Establishment of Linters Grades

A. Historical

Until the beginning of World War I, the nature and qualities of cotton linters had been given very little attention. The cottonseed crushing industry was just beginning to recognize this by-product as a possible additional source of revenue. During the season of 1911-12, only about 556,000 bales of linters were produced. The European demand for linters as a source of cellulose for the manufacture of smokeless powder caused a gradual increase in production, until during the season of 1914–15, some 832,000 bales were produced. With the entrance of the United States into the war, the War Industries Board urged the mills to produce even more. In response to this urging, the crushing mills, during the season of 1916–17, produced 1,310,163 bales while processing 4,479,176 tons of cottonseed—or an average recovery of 149 pounds of linters per ton of seed. However, in the effort to achieve increased production, little attention was given to the quality of the product. The result was that approximately 20% of the linters produced could not be used for war purposes because of their poor quality and, moreover, had no peacetime use.

The enormous increase in the recovery of linters, coupled with developments in the uses and demand, gradually took the production of linters out of the "waste" class and gave it the character of a special industry. This condition eventually resulted in the passage of a resolution by the Interstate Cotton Seed Crushers' Association at its convention held in May, 1924, requesting the Department of Agriculture to determine and

establish standard grades for American cotton linters. The author was designated to make a special study of linters with the view of formulating a grading system.

Special committees were appointed by associations of the cottonseed crushers, mattress manufacturers, and linters dealers to assist in the project. In fact, valuable assistance was granted by all branches of the industry. Many conferences were held at which ideas as to grading and the difficulties encountered in the trading of linters were thoroughly discussed. All classes of consumers furnished the Department with samples of linters of the types each preferred. A number of dealers provided sets of types used by them in trading. After the opening of the cottonseed crushing season of 1924–25, samples were furnished by representative crushing mills located in every section of the Cotton Belt. Some mills sent in samples weekly throughout the season, so that variations in quality might be studied. These studies led to the conclusion that there were four factors influencing the grade or value of linters. These are: staple, content of foreign matter, color, and character.

B. Factors Influencing Grade

1. Staple

In describing linters, the term "staple" is used with reference to the different blends or the preponderance of one or the other of the two types of fiber of which linters is composed. Although different degrees of intensity in delinting process and variations in the total residual fiber in different lots of seed make possible all degrees of variation in the mixtures or in the blends of these two types of fiber, each special channel of consumption is very definitely limited to comparatively narrow variations in the blends.

2. Foreign Matter

Foreign matter in linters consists of broken leaves, motes, sticks, dirt, and particles of the seed coat or hull that have been rasped off by the delinting saws, and the quantity present is influenced by the care exercised in cleaning the seed. The nature of the foreign matter varies in the different geographic sections of production. Foreign matter in linters produced in the Southeast is likely to consist chiefly of very fine particles of the seed coat, known as pepper trash. The particles of seed coat or hull in linters produced in the Mississippi Valley States are usually larger than in linters produced in the southeastern States. Linters produced in Texas and Oklahoma are usually rather free of pepper trash, but frequently contain more large pieces of hull, broken leaves, and carpels than are found in linters from other sections.

3. Color

The natural colors of linters are various shades of olive and buff. During exposure to light, the olive coloring sometimes shades off through a light buff or cream to a deep buff. In trade parlance, these colors are usually spoken of as green, cream, and reddish. Olive prevails in Southeastern and Valley linters, and light buff to buff in Western and Southwestern linters. Natural colors are easily bleached. However, other colors are sometimes found in linters. These are usually the result of weather damage or fungous staining of the fiber, either while it is still on the undelinted seed or after it has been delinted and baled. Such colors might be called unnatural colors and are difficult or impossible to bleach.

4. Character

In describing the quality of linters, three types of so-called "character" are recognized and are designated, respectively, as "Western," "Valley," and "Southeastern." Character in linters is a term used to cover a combination of three elements: maximum length and uniformity in length of the long fibers, softness or harshness (resiliency) of the mass of fibers as a whole, and smoothness or neppiness. Character in linters is apparently a sectional characteristic, and is probably influenced by soil and seasonal conditions and by the prevailing varieties of cotton planted. Linters of Western character are harsh, resilient, and usually neppy; and the long fibers are comparatively short, but regular in length. Linters of Valley character are soft. The long fibers are the longest found in linters, but usually are irregular in length. Valley-character linters are frequently neppy, but not so distinctly neppy as linters of Western character. Linters of Southeastern character are comparable to linters of Valley character in softness, but are smoother and less neppy; the long fibers are intermediate in length between those of Western and Valley characters and are more uniform in length. In general, both Valley and Western characters appear to result from an intimate mixture or blending of the long fibers and fuzz. Linters of Southeastern character are distinctly different in this respect from linters produced in the other two regions, being filamentous in appearance, as if made up of fine laminations of the long fibers and the fuzz. Although both the color of linters and the character are usually associated with certain producing sections, at times linters of either the character or the color usually associated with one section are produced in the other sections.

C. Classes of Consumers

The consumers of linters may be divided into three general groups, consisting of spinners, felters, and chemical users. The quality of the linters used by each of these groups varies and overlaps. Utilization is

based primarily on the relative proportions of the two types of fibers present.

The chemical users are the largest single consuming group. As produced at the mill, linters contain from 70 to 85% of available cellulose. By chemical purification, this is increased to about 98%. Among the products made from purified linters are rayon, plastics, explosives, and lacquers. The next largest consuming group is composed of the felters who prepare linters for use in mattresses, in furniture, and in automotive upholstery. In some instances, the manufacturers of the end products produce their own felts. Linters containing the largest proportion of long fibers are spun for use in the lower grades of cloth, wicks, and twine. They are also bleached and sterilized for use as absorbent cotton.

D. The Present Grading System

1. Establishment of Numerical Grades

Most of the systems used for grading agricultural products are based primarily on the extent to which the product is damaged or on the content of extraneous matter; but in devising a grading plan for cotton linters, a new concept [1] of grading was used. This consisted of making grades meet the preferences of each type of consumer, each grade to have a tolerance of foreign matter consistent with the amount found in linters manufactured by a well-operated and efficient cottonseed mill. The following scheme of grading was accordingly recommended. There were to be seven basic grades ranging from the highest quality of linters usually produced down to the lowest quality; the seven grades were to cover all qualities produced. Each grade was to be represented by a series of 12 standard reference samples, placed in a box in three tiers. The samples were to be numbered consecutively from the upper left hand sample down to the lower right hand sample. Samples numbered *1*, *2*, *3*, and *4* in each box were to represent the character of linters produced in the southeastern States; samples numbered *5*, *6*, *7*, and *8* were to represent the character of linters usually produced in the Mississippi Valley States; and those numbered *9*, *10*, *11*, and *12* were to represent the character of linters usually produced in the western States. The samples in each tier were to grade down from left to right. Samples numbered *1*, *5*, and *9* in each of the lower grades were to be approximately equal in quality to samples numbered *4*, *8*, and *12* in the next higher grade. The gradations were to be based on the proportions of the long fiber and fuzz fibers, with a slight increase in the amount of foreign matter to be permitted with decreasing grade. Each box as a whole was to show the expectant variation both in the character

[1] Report of Rules Committee, 29th Annual Convention, Interstate Cotton Seed Crushers' Association, in *Cotton Oil Press*, **9**, No. 2, 36 (1925).

of the fibers and in the amount of foreign matter generally to be found in bales of linters turned out by carefully managed mills.

As indicated above, the grades were based on the relative proportions of the two types of cotton hair or fibers. Thus grade *1* is composed of linters in which a very large portion of the long type of fiber is present, while grade *7* consists of linters in which the short type or fuzz fiber predominates and in which practically all of the long fibers present have been cut or broken.

The proposed grades, having been approved by the Interstate Cotton Seed Crushers' Association [1] (now the National Cottonseed Products Association), by the Better Bedding Alliance of America, and by various dealers and brokers, were promulgated by the Secretary of Agriculture [2] as tentative standards which would become effective as mandatory standards under the provisions of the United States Cotton Standard Act on August 1, 1926.

2. Subdivision of the Official Grades

When the standards were first established, there was some complaint from the trade that the individual grades were too narrow in range of qualities. However, through the use of the standard grades as guides, and through improved methods of collection and baling, linters of such uniformity were later being produced that the complaint changed from "too narrow" to "too wide," and requests were received that the standard grades be subdivided for trading purposes.

The arrangement of samples and characters enables the official grades to be subdivided for trading purposes directly into the three characters—and, whenever expedient, by reference to the number of the sample and grade, down to individual samples or combinations of samples.

In May, 1928, on the recommendation of the Committee on Standardization of Linter Grades, the N.C.P.A. adopted trading rules that provided for the subgrading of the standards, that is, each of the seven standard grades was to be divided into three subgrades: high, middle, and low; and provision was made for basing contracts for the sale of linters either on a full grade or on any subdivision of a standard grade.[3] The Department of Agriculture soon after amended its regulations so as to recognize not only the subdivisions adopted by the industry, but also to give standardized terminology to any combinations of quality not exceeding the limits of a compound grade as established when the standards were promulgated.

[2] U.S. Dept. Agr., *Service and Regulatory Announcements*, No. 94, July 7, 1925.
[3] Report of the Rules Committee, 32nd Annual Convention, Interstate Cotton Seed Crushers' Association, in *Cotton Oil Press*, **12,** No. 2, 32–33 (1928).

3. Board of Cotton Linters Examiners

On December 11, 1926, the regulations of the Secretary of Agriculture under the Cotton Standards Act were amended to provide the same governmental facilities and services for cotton linters as were available for cotton. Under this amendment, a board of cotton linters examiners was established in Washington, D. C., consisting of three members, with power to certify the grade and character of such samples and bales of linters as might be submitted for the purpose.

Provision also was made for the licensing of competent persons to grade and classify linters and to certify the grade or the class in accordance with the official standards of the United States for American cotton linters.

4. Establishment of Color Standards

In the promulgation of July 7, 1925, mentioned above, three of the four principal factors of value in American cotton linters were standardized, *i.e.*, characters, staples or blends of fiber, and content of foreign matter.

After a conference held in Memphis, Tennessee, on October 6, 1927, representatives of the linters industry requested that the Department of Agriculture establish standards for the remaining factor of value—color—and that the normal color of linters, as carried in the samples used in constructing the original standard grades, be established as standard. This request was complied with in a public notice issued by the Secretary of Agriculture and dated October 31, 1927.

Copies of the standard grades for American linters are prepared by the Department of Agriculture and sold to the trade in the same manner as are copies of the cotton standards. Because of the vicissitudes of use, including the probability of alterations in these copies, the valid life of copies has been limited to one year from the date of issue.

5. Expositor Type Standards

On March 25, 1927, a meeting was held at Memphis, Tennessee, at the request of the Committee on Standardization of Linter Grades of the Interstate Cotton Seed Crushers' Association, to which were invited representatives of the Mattress Manufacturers Association, the chemical users of linters, linters dealers' associations and exchanges, and cottonseed crushers. The purpose of the meeting was to discuss the sufficiency and the increased utilization of the standard grades.

During the conference, it was disclosed that both the construction of the grades and the method of preparation of the samples were entirely new to the industry. The Department of Agriculture was accordingly requested to furnish holders of copies of the standard grades with small

loose samples illustrating the characters and staples as represented in the standard grades, so that they might better acquaint themselves with the standards. This the Department agreed to do, with the understanding that the samples so furnished would be used for informative purposes only, and would not be used as standards.

6. Utility of the Quality Standards [4]

Heretofore, grades *1* and *2* have generally been called "first-cuts." The samples in grade *3* have been called "first-cuts" by some and "mill-runs" by others. Grade *4* is composed of samples heretofore generally known as "mill-runs." Grade *5* is composed of samples heretofore known as "mill-runs" and "second-cuts." Grades *6* and *7* are composed of samples heretofore known as "second-cuts."

The standard grades for American cotton linters cover all qualities of linters that are carefully prepared; they may also be used for the classification of bales of linters that are poorly prepared (that is, bales that contain more foreign matter than the tolerances shown in the standards) by comparison with the standards on the basis of the blends of fibers, and the assessing of discounts according to the excess of trash that they may contain.

The standard grades have been recognized in the trading rules of the industry; however, the mills have been slow to change their marketing practices. They sell linters ostensibly on sample, but actually subject to inspection and acceptance by the buyer. Under this system, on a rising market the mills are assured of the quick removal of their stocks, quick settlement, and reduction in storage. However, on a declining market, under an inspection and acceptance system, rejections increase and acceptances are slowed. It is under such conditions that definite standards of quality will be found most useful. A further use of the standards and one which is at present perhaps the most important is that of linters quality control by the mills during production.

The group of users comprising spinners and felters, who use grades nos. *1* to *4*, inclusive, have heretofore secured their supply of raw material through the inspection and acceptance of samples offered by dealer's agents on personal visits. As a result, it was not until price ceilings, based on the standard grades, were established early in World War II by the Office of Price Administration that this group began to utilize the quality standards. It is the author's belief that a majority of these consumers of linters now think of the qualities of linters in terms of the standard grades, even though they may still make their purchases largely on the basis of samples exhibited to them by dealer's agents.

[4] For additional comment on the present system of linters grading, see Chapter XVI, page 668.

Among the chemical consumers, those using linters as a filler of plastic articles are interested in the use of the standard grades. But the large consumers of linters as a source of cellulose, because of the special and peculiar chemical qualities of their products, make their purchases after inspection and acceptance by their own agents, with settlement on the basis of the cellulose content (see page 899). However, during World War II the use of the standard grades as guides in the production of linters by the cottonseed mills resulted in the maintenance of such high quality

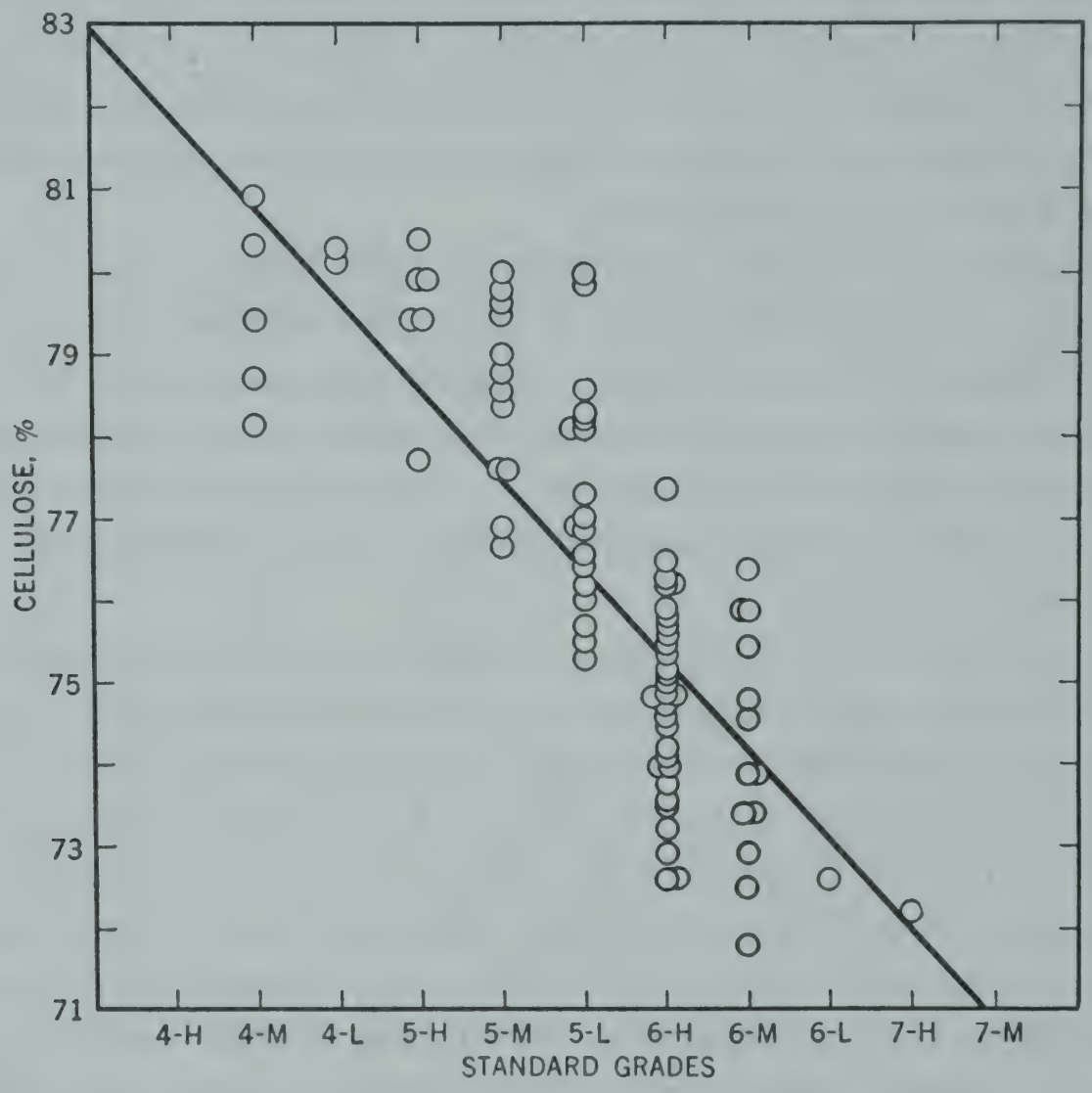


Fig. 120. Correlation between standard grades and cellulose content of linters. Each circle represents the average of the season's production of a crushing mill.

in the linters that were produced for cellulose that less than 1% was rejected on account of off quality, and only about 2% were unsuitable because the grade was too high for satisfactory chemical use—the staple being too long.

During the war, the War Production Board required the cottonseed crushing industry to sell for chemical purposes from 65 to 100% of the linters produced. The percentage varied during different periods in accordance with changing military needs. For war purposes, the cellulose content of the linters was the chief factor of value. Since the standard grades for linters were based on blends of fibers without reference to the cellulose

content, all of the supply purchased for war purposes was bought on the basis of cellulose content. The Office of Price Administration set a ceiling on the basis of what was believed to be the average cellulose content, 73%, with premiums and discounts being based on variations in cellulose above and below this figure.

In order to assist the crushing mills to produce the greatest quantity of linters of the highest quality, the War Production Board requested that each mill send samples weekly to the U.S. Board of Cotton Linters Examiners for appraisal as to quality. Not only was advice given as to quality from the standpoint of freedom from dangerous or uneconomical forms of foreign matter, but the samples were also classified on the basis of the standard grades. Later the cellulose content, as determined by chemical analysis, was correlated with the standard grades.

An examination of samples representing 130,000 bales produced during the 1944–45 season showed an average of approximately 72% cellulose for linters grading 7-High with a gradual increase up to approximately 81% for linters grading 4-Middle. On the basis of these analyses, a positive correlation between the standard grades and the cellulose content can be observed (Fig. 120).

7. Notes on Sampling

The diversity of methods employed in the baling of cotton linters makes it pertinent to mention a few precautions to be observed in sampling of the bales. Three general methods are used in the baling of linters. These methods and the sampling procedures appropriate to each are as follows.

(*a*) Each individual delinting machine is equipped with a condenser from which linters are doffed onto a spindle. When the roll or bat on a spindle reaches a weight of between 15 and 25 pounds, the bat is removed and placed in a bale box. When from 30 to 40 bats are in place in the box, they are compressed and wrapped into bales weighing approximately 600 pounds each. Each of the bats may differ in quality or grade from the other bats in the bale, so that a sampler should examine the ends of the bats in the head of the bale and draw portions (4 or 5 inches square) from several bats so as to insure a sample showing the full range of qualities in the bale. (Caution: high-grade bats after compression frequently protrude so as to cover the ends of low-grade bats.)

(*b*) Each delinting machine is equipped with its individual condenser, but when the condensers are doffed the linters are dropped on to a traveling belt which conveys the material to the bale box for compressing and baling. Bales of linters so formed are made up of comparatively small wads of linters of various qualities. The sampler should see that the sample drawn contains portions of the various qualities in approximately equal parts.

(*c*) A battery of delinting machines may be equipped with a common lint flue and condenser, just as is a battery of gins. This method of collection results in a blending of the qualities produced by the several delinting machines, so that a fair sample (5 or 6 ounces) should represent all qualities.

Samples may be drawn without cutting the bagging. The preferred practice is to use a bale hook, which after insertion should be turned slightly and then used to pry out portions of the linters.

D. COTTONSEED PROCESSING

CHAPTER XIII

HANDLING AND STORAGE OF COTTONSEED

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I. Introduction

In the early days of the industry and as late as 60 to 65 years ago, the disposal of excess cottonseed was a considerable problem. The excess seed were used as fertilizer, burned, thrown into streams or bays, or allowed to rot around the gins. To protect the public from the very foul odors of decaying proteinaceous material and the generally unsanitary conditions resulting from such practices, it was necessary to enact health laws prohibiting the "dumping" of cottonseed. The transition from these crude methods of handling and disposing of cottonseed to the present controlled methods is an interesting development.

The handling and storage of cottonseed is one of the most important phases of cottonseed processing. It is so important to the profits of the oil miller that he should assign only the best personnel to supervise these operations. As an example, we may consider the case of one 4,000-ton lot of seed in a house or tank which has been purchased at the current base price of $56.00 per ton. This means a raw material investment of over a quarter of a million dollars. A rise in free fatty acids of the oil amounting to 1% results in the reduction of *value of oil* to the processor as follows: in seed containing up to 2% FFA as received, about $00.63 per ton, or a total of $2,520; in seed above 3% FFA as received, about $00.84 per ton, or a total of $3,360. This is "important money" to any cottonseed miller.

Cottonseed are a very perishable commodity, particularly when the moisture of the seed exceeds 10 to 11% and inadequate storage facilities are available.

Table 168, page 615, shows the growth of the cottonseed crushing industry in the United States and the number of mills processing the seed. In the 1944–45 season, 4,253,000 tons were crushed in 382 mills. These mills ranged in capacity from about 25 to about 450 tons per day. Their crushing season varied from just a few weeks' operation to continuous full-year operation.

This wide difference in processing practices from mill to mill results in corresponding differences in handling of the seed as received at the mill, as will be discussed later.

The normal cotton harvesting season extends from August through December with some straggling harvesting occurring after January 1. Table 160 shows cottonseed receipts at mills by months for the 10-year

TABLE 160

Cottonseed Tonnage Received by Mills in the United States According to Months, Crop Years 1936–45[a]

Month	10-year average receipts, tons	Percentage of total received in the month	Cumulative percentage
August	220,798	5.0	5.0
September	1,048,217	24.0	29.0
October	1,267,907	29.0	58.0
November	785,388	17.9	75.9
December	409,927	9.4	85.3
January	233,632	5.3	90.6
February	149,866	3.4	94.0
March	98,777	2.3	96.3
April	47,233	1.1	97.4
May	38,737	0.9	98.3
June	35,419	0.8	99.1
July	37,581	0.9	100.0
Total	4,373,482	—	—

[a] U.S. Bureau of the Census, *Cotton Production and Distribution.*

period 1936–45. It is seen that normally 80% of the seed are received at the mills during four months, September to December, inclusive, and up to 85% are normally received by January 1. Until the past few years, most of the seed moved to the mills by rail. Now about 80% of the total is hauled by trucks.

II. Handling of Cottonseed at the Gins

An average boll of cotton contains about 40 seeds. From the moment the boll bursts open on the stalk, the seed are subject to deterioration. Subsequent exposure of the boll to various weather conditions, such as rains followed by little sunshine, frost, etc., will cause serious damage to the kernel in the seed and generally affect the quality of the cotton and the lint. Since cottonseed are an extremely perishable commodity, it is obviously to the advantage of the farmer, the ginner, and the oil processor to have the cotton bolls picked as promptly as possible, with a minimum exposure of the seed cotton to wet weather.

With desirable dry weather conditions, the seed as ginned normally contain less than 11% moisture and the free fatty acid content of the oil

in the seed is normally of the order of 0.5 to 1.0%. Under these conditions, the seed can be stored temporarily at the gin, in relatively small quantities, with little deterioration. When, however, the seed moisture is above 10 to 11%, there is much danger of heating in a seed pile, with accompanying rapid deterioration. Early in the season, with normal high atmospheric temperatures often well above 90° F., the temperature of the seed as they go to storage is dangerously high, so that heating will start quickly if the seed are moist.

A considerable number of gins have installed seed cotton dryers. This drying equipment is designed to remove moisture from the cotton to facilitate fiber removal. The effect on the moisture content of the seed itself is relatively small, there being a reduction of only 0.6 to 0.7%, as reported by Rusca.[1] However, drying seed cotton before ginning at temperatures from 160° to 220° F. is reported to retard the formation of free fatty acids in the stored seed.

The great bulk of cottonseed is shipped promptly from the gins to the mills with relatively little additional deterioration occurring in the seed. In modern gin installations, the seed are stored on the second story of the seed building from which they can be dropped directly into trailer trucks or conveyed to railroad cars with little labor.

It is desirable to have equipment available at the gins for the rapid determination of seed moisture. Equipment like the Steinlite moisture tester or similar instruments, which depend upon electrical conductance through a mass of seed, give sufficiently accurate results (usually within $\pm$ 0.5% of the true value).

During periods of wet weather particularly in August and September, a considerable amount of "hot" seed is received at the mills in rail shipments. Many of these lots of high-moisture seed have started heating at the gin or during transit. Storage of 25 tons of wet cottonseed in a closed box car which is exposed to the hot sun during transit frequently results in rapid heating and souring. Often, cars of seed are received so hot that the hand cannot be thrust into the seed mass. Such seed have a sour, acetic acid-type odor and are undergoing rapid deterioration.

Lots of seed are occasionally held too long at the gins in "corner piles" or are held while the ginner waits for a better market. These seed often will go through a slow heating process, so that the meats as received at the mill are discolored from brown to black. Seed of this quality have relatively little value, as they yield products—lint, hulls, meal, and oil—of off quality. The free fatty acid content of the oil may rise to as high as 20 to 40%, and refined oil colors may be anywhere from 50 to 120 Lovibond red units.

If the *minimum* values quoted above are assumed, *viz.*, 20% FFA and

[1] R. A. Rusca, *U.S. Dept. Agr. Bull.*, **651** (1942).

40 red refined color, the oil dockage to the processor at the current market value of prime crude oil ($0.20 per pound) is over $0.09 per pound, which is equivalent to over $27.00 per ton of cottonseed. In addition, he will suffer a marked reduction in the oil yield and also quality discounts on lint, hulls, and meal. These examples of marked reduction in value resulting from deterioration show that seed should be moved to the oil mills as promptly as possible, since the mills are generally equipped to store seed in such a manner that a minimum amount of spoilage will result.

III. Handling of Cottonseed at the Mills

A. Problems in Receiving the Seed

Cotton oil mills receive seed from territory within a radius of 10 to 100 miles or more of the mill. It is very likely, therefore, that seed with marked differences in quality will be received by a single mill. For example, one section may have been affected by a severe storm, the tail of a hurricane, with resulting field damage to the seed, while other adjacent sections will have less damaged seed or perfectly prime seed. For proper handling and segregation of these seed, the mill must be equipped and organized to collect the analytical information on the seed quickly, so that they can be routed to the proper storage bins.

Seed received at the mills by rail offer relatively little difficulty in handling. The car can be sampled when it arrives in the railroad yard, and the analysis for moisture, free fatty acids, and foreign material made available before the car is spotted. With over 80% of the seed at present being received by truck, however, the proper handling can become very complex.

The estimated time required to weigh, spot, sample, and unload an

TABLE 161

Minimum Time Required to Unload Cottonseed Received in Trucks[a]

Maximum daily mill receipts, tons	Number of trucks unloaded per 24 hours	Unloading station number			
		1	2	3	4
		Time to unload, hours			
200	25	8+	—	—	—
400	50	17	8+	—	—
600	75	—	13	8+	6+
800	100	—	17	11	8+
1000	125	—	21	14	11
1200	150	—	—	17	13
1400	175	—	—	20	15
1600	200	—	—	22	17
2000	250	—	—	—	21

[a] Average truck load, 8 tons; unloading time, 20 minutes.

8-ton truck load of cottonseed is about 20 minutes using a power shovel or pneumatic unloader. Table 161 shows the number of unloading stations required by a mill to handle various daily receipts. It also indicates the magnitude of the sampling problem.

When one considers, that a majority of the trucks move during daylight hours, and that there is a real advantage to the trucker if he encounters a minimum of waiting time, it is evident that the seed handling organization at a mill must be well-trained and alert to properly route the daily receipts when the "great seed movement" is on.

Many of the larger mills require several seed unloading stations, and for proper seed segregation, these should be able to send seed to various storage units. However, this desirable flexibility cannot always be obtained and many compromises must be made.

B. Analysis of Seed for Selective Storage

Reference to Table 161 will also show the size of the sampling and analytical crew necessary to produce prompt analytical information. Each truck must be sampled by one of the official methods prescribed by the U.S. Department of Agriculture (see pages 574–575). About 2 pounds per ton of seed are drawn, collected, and stored in an authorized container under proper shelter. When about 50 pounds of seed have been collected, representing 25 tons from a shipper, the sample is "cut," cleaned, and reduced over an approved shaker. A gallon sample is certified by the sampler and labeled to show the per cent foreign material removed by the shaker. These samples are sent to official seed grading laboratories and settlement for the seed is made on the basis of the analyses.

In addition to these official samples, a second similar set of samples is drawn at some mills for accounting and storage information. "Shipper" records are kept which show the analyses of the previous samples. The important information for proper segregation of seed to storage is per cent moisture and per cent FFA in the oil in the seed. Facilities for the rapid determination of moisture by an electrical apparatus are available at some mills. When seed moistures are very high, this equipment is used to determine quickly the moisture content of seed on each truck. A moisture determination with a moisture meter can be made in less than 5 minutes and the results are acceptably accurate. Rapid analyses for FFA on many samples are not practical. It is possible to determine the FFA on one or two samples in about 20 minutes, but it is not practicable from the point of view of analytical manpower to do this continuously. Also, a result after 20 minutes is of little value, since a truck cannot be delayed for this length of time. It is necessary, therefore, to rely on previous "shipper" analyses for routing of the seed. This result in an occasional seed truck going to the wrong storage unit, but this happens infrequently, since the

quality of the seed from the same shipper normally does not fluctuate a great deal.

C. Methods of Unloading

The four types of unloading equipment in general use in the industry will be described in the following sections.

1. Unloading Car Seed into Side Conveyors

A metal chute is placed between the car door and a conveyor. The seed are either forked by hand into the conveyor or unloaded by means of a power shovel. The application of the power shovel is the same as in the following description of power shovel unloading of truck seed.

2. Power Shovel Unloading of Truck Seed

With a single-unit power shovel, it is possible to unload about 30 tons of seed per hour using two operators. The operators remove the end gates, alternate in unloading the truck, sweep the truck, and replace the end gates. Figure 121 shows the unloading of cottonseed by means of a power

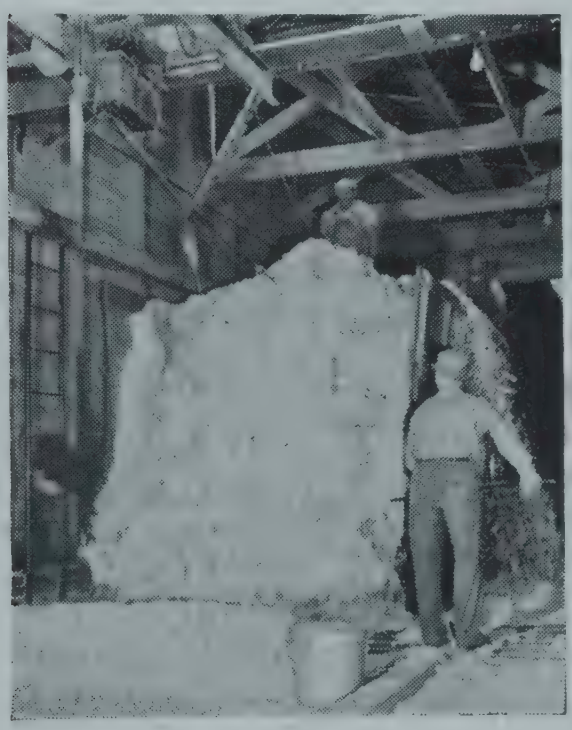


Fig. 121. Power shovel unloading of cottonseed.

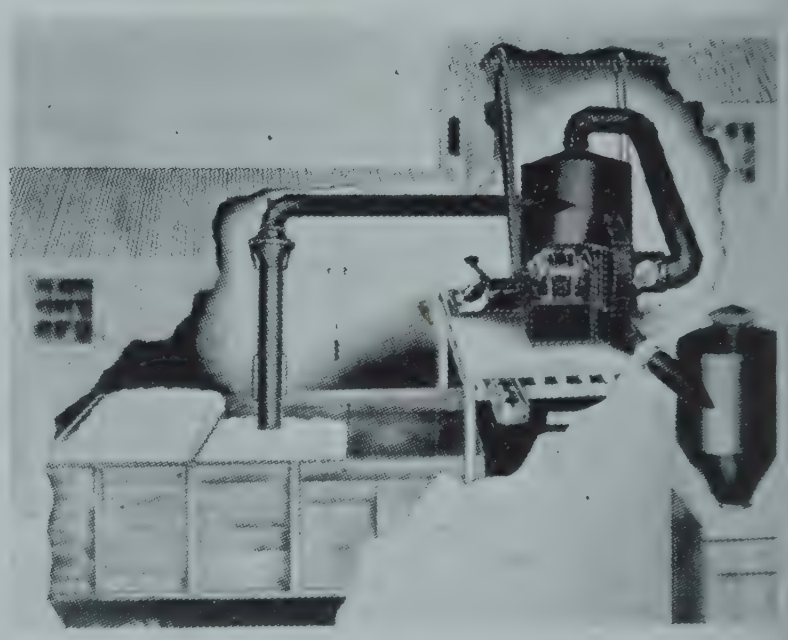


Fig. 122. Pneumatic cottonseed unloader.

shovel. The "shovel" proper is a light-weight aluminum plate about 30 × 30 inches in dimensions, with handles. To it is attached a steel cable from a power drum. The operator pulls the shovel to the rear of the load, unwinding the cable from the power drum. When he is ready, he pulls a cord which causes the motor and drum to engage and thus wind up the cable and pull the seed out the end of the truck.

About 15 minutes are required to unload an 8-ton truck after the end gates have been removed. The time required to remove and replace the end gates on all kinds of trucks is one of the time-consuming operations.

Figure 121 shows also a seed sampler drawing an official sample of seed from the falling stream. An elevator bucket attached to a steel rod is being used. The seed sample is placed in the sample can shown and then transferred to a heavy-weight can of 2½-bushel capacity with a close-fitting cover, and is protected under a shelter from sunlight and rain. About 50 pounds of seed are collected in the large can, representing 25 tons of cottonseed.

This type of unloading equipment has the advantage of low operating cost and a relatively low installation cost. Its chief disadvantage is in the long time required to remove and replace the end gates from various trucks.

3. Pneumatic Seed Unloading

A typical pneumatic cottonseed unloader is depicted in Figure 122. This type of unit has a capacity of 30 tons of cottonseed per hour. The seed are removed from trucks or wagons by the movable suction nozzle, which is moved back and forth over the surface of the seed by the operator. Since the seed are unloaded by air, they are cooled and dried somewhat. Considerable dust and heavy trash is also removed from the seed during the operation. Seed truckers generally like this equipment because it does not necessitate removal of end gates and thus is easier on their trucks. Normally two men are required to unload seed. The power cost for operation of a pneumatic unloader is high (75 h.p. connected load), and the installation cost of this type of unloading equipment is likewise relatively high.

4. Truck Dumper Unloading

A truck dumper seed unloading installation is shown in Figure 123. This equipment has been used successfully for years in grain elevators to unload grain from trucks and wagons. Some installations have been made at cotton oil mills, and the units are reported to be operating successfully even with large trailer trucks. The trucks are chained to the platform, which is then elevated by hydraulic pressure. The seed flow out the back of the truck when the platform is inclined about 40° from a horizontal plane. The main advantages of this type unloading system are the speed of unloading and the low operating cost. Its installa-



Fig. 123. Truck dumper cottonseed unloader.

tion cost is relatively very high and it also requires end gate removal from trucks.

D. Sampling of Cottonseed

Cottonseed purchased on standard grades of the U.S. Department of Agriculture are sampled by persons licensed by the Secretary of Agriculture. Each sampler should have the following tools available:

(*1*) Suitable sampling forks or triers.
(*2*) Metal containers with close-fitting covers, 2½-bushel capacity.
(*3*) Friction-top cans, 155-cu. in. capacity.
(*4*) Scales graduated in ounces or half ounces.
(*5*) Shaker cleaner provided with a sample reducing device.
(*6*) Suitable thermometer.
(*7*) Corkscrew-type with a 2-in. pitch to form an open cylinder 3–4 inches in diameter, and about 48 in. long.
(*8*) Unloading sampler consisting of an $8 \times 5 \times 5\frac{1}{2}$-in. elevator bucket attached to a long pole.

1. Sampling of Railway Cars

A car may be sampled at approximately 10 locations with the corkscrew trier, if the car is not too full. When the car is filled, it may be sampled by digging a hole 30 inches deep with a short-handled 5-tine fork in each of the four quarters of the car. About 15 pounds of seed are taken from the bottom and sides of each hole. They are placed in moisture-proof bags and transferred immediately to the 2½-bushel metal container.

Cars may be sampled as unloaded by use of the elevator bucket sampler, mentioned under (*8*) above. The sampler is placed in the center of the stream of falling seed from the car at regular intervals. Approximately 2 pounds of seed are drawn per ton of seed unloaded. The sample as drawn is placed in the 2½-bushel metal container. Not less than a 50-pound sample is taken from each car.

2. Sampling of Trucks or Wagons

Cottonseed from trucks or wagons are sampled exactly as described above for partially filled railway cars. The total weight of the sample taken is not less than 2 pounds per ton of seed. The sampler records the actual temperature of hot car or truck seed by obtaining readings near each end of the car and the center of the truck.

For additional data on cottonseed sampling see pages 507–512.

3. Handling of Samples

The entire original sample in the 2½-bushel metal container is weighed and passed over the approved shaker cleaner. The cleaned seed or the

removed foreign material is weighed to enable calculation of "Per Cent Foreign Material."

Most shaker cleaners are equipped with a sample reducing device, otherwise the seed must be mixed with a MacLellan mixer. An official cleaned sample of not less than 2 pounds is packed into a friction-top can. A sampler's certificate is enclosed and the sample is sent to an official chemist for analysis and grading.

Samples are required as follows: (*a*) for each carload, (*b*) for each 25 tons delivered by truck or wagon within 3 consecutive days, and (*c*) for lots less than 25 tons, but not less than 10 tons received within 3 consecutive days. At the beginning and end of seasons when deliveries of seed are slow, samples from individual shippers may be held up to 7 days in metal containers with close-fitting covers. A duplicate sample in a friction-top can is held by the sampler until the analysis and grade have been received.

A cottonseed sampler's certificate (shown below) properly filled out is enclosed with each sample.

COTTONSEED SAMPLER'S CERTIFICATE

Date sample was drawn*_____ to _____

Identification of shipment _____

Point of origin_____ County_____ State

Weight of original sample_____ lbs._____ ounces

Net weight of cleaned seed_____ lbs._____ ounces

Weight of foreign matter_____ lbs._____ ounces

_____

(If seed are hot give temperature.)

_____

I hereby certify that the accompanying sample of cottonseed is the OFFICIAL SAMPLE representing the lot of cottonseed marked or identified as above and that the drawing and preparation was done in accordance with the methods prescribed in the Rules of the National Cottonseed Products Association, Incorporated.

(Signature)_____

*If the official sample represents wagon or truck deliveries covering more than one day give the inclusive dates.

For analysis and grading of cottonseed, see Chapter X, pages 512–522.

The official chemists often indicate, *for information only,* the estimated yields of oil and cake per ton of cottonseed based on standard milling efficiency.

IV. Treatment of Seed Prior to Storage

A. Drying Cottonseed

Cottonseed dryers have been in use in cotton oil mills for many years.[2] Figure 124 shows a cross section of a typical dryer. The seed flow through the dryer as 6-inch ribbons; they are dried at about 220° F. in the drying section and cooled to within about 15° F. of atmospheric temperature in the cooling section.

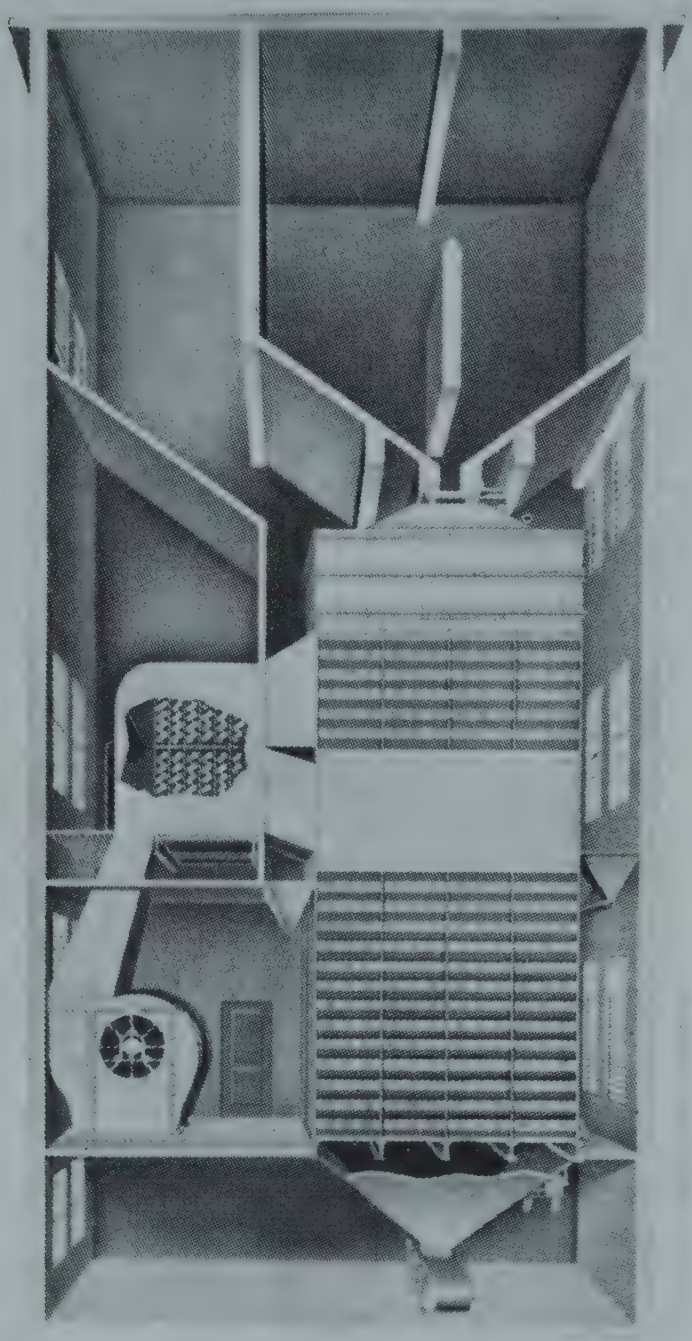


Fig. 124. Cross section of Hess dryer for cottonseed. (Courtesy *Hess Warming & Ventilating Co.*)

The capacity of the dryer will vary depending on the amount of drying to be done. Table 162 shows the capacity of a large Hess dryer when operated to remove varying amounts of moisture from cottonseed.

Often it is desired to remove only a few per cent of moisture from exceedingly wet seed, in order to obtain greater drying capacity and still dry the seed to a safe level for storage in air-cooled units. Whenever possible, the seed should be dried to a 10–11% moisture level for safe storage. Dryers are very serviceable in lowering the temperature of hot seed containing about 12% moisture. The seed as unloaded are passed through the dryer, with no steam on the coils but with the fans operating.

The cost of drying cottonseed varies with the daily tonnage dried, the prevailing wage rate, the cost of power and fuel, and overhead costs, as determined by the total tonnage dried per year. Normally, when the dryer is operated at the rate of 300 to 500 tons per day and about 8,000 tons per season, the drying cost varies from about $00.75 to $1.00 per ton. The cost is high because the investment in the drying equipment is very large; the capacity of the dryer must be relatively large to handle peak loads. Also, during many seasons, the dryer is not needed, so the unit stands idle. Cottonseed dryers are excellent "stand-by" insurance for emergency handling of very wet seed.

[2] G. B. Alford, *Cotton Oil Press*, **5**, No. 5, 41 (1921).

TABLE 162

Dryer Capacity in Tons of Cottonseed per 24-Hour Day

Initial moisture, %	Dryer capacity (tons) for various reductions in moisture								
	2%	3%	4%	5%	6%	7%	8%	9%	10%
12	528	—	—	—	—	—	—	—	—
13	554	374	—	—	—	—	—	—	—
14	590	398	302	—	—	—	—	—	—
15	622	420	319	257	—	—	—	—	—
16	653	439	334	269	228	—	—	—	—
17	679	458	348	281	238	206	—	—	—
18	708	478	362	293	247	214	190	—	—
19	734	497	377	305	257	223	197	178	—
20	761	514	391	317	266	230	204	185	168

B. Precleaning of Seed

Until recently, it was often the practice of some ginners to return all of the bolls, sticks, and trash removed from the seed cotton during ginning to the cottonseed. There has been much criticism of this indefensible practice, particularly during the war years. This trash is very hard to remove and is very objectionable when it finds its way into linters and therefore eventually into guncotton and other linter products.

Numerous authors have pointed out the advantages of precleaning cottonseed before storage.[3] Bolls, burrs, cotton stalks, etc., are high in pentosans which will contribute to heating of the seed and also to discoloration of the linters. While it is generally agreed that removal of foreign material from cottonseed is desirable before storage, no practical means of removal has been devised by oil mill process engineers. Cottonseed are received at mills in quantities so large during the normal seed movement that it would require equipment of enormous size to clean the seed. So far, no economic solution has appeared.

V. Types of Storage Units

There are 2 types of seed storage units in common use at oil mills today: seed houses and silos. Both have been described repeatedly in the literature.[4] A recapitulation of their distinguishing features follows.

A. Seed Houses

The older seed houses were built of wood and were composed of a series of bins, each having a seed capacity of from 100 to 1,000 tons. These units were built both with and without seed cooling facilities.

[3] C. S. Brust, *Cotton Oil Press,* **10,** No. 5, 25–26 (1926). C. L. Locket, *ibid.,* **10,** No. 3, 29–30 (1926). R. Y. MacIntyre, *Cotton and Cotton Oil Press,* **38,** No. 25, 3–5 (1937). M. K. Thornton, Jr., *Cottonseed Products,* Oil Mill Gazetteer, Wharton, Texas, 1932, pp. 31–39.

[4] See, for example, O. Adams, *Oil Miller & Cotton Ginner,* **34,** No. 5, 13 (1929), and H. F. Cornwall, *Cotton Oil Press,* **2,** No. 2, 22–23 (1918).



Fig. 125. Muskogee-type cottonseed storage house.

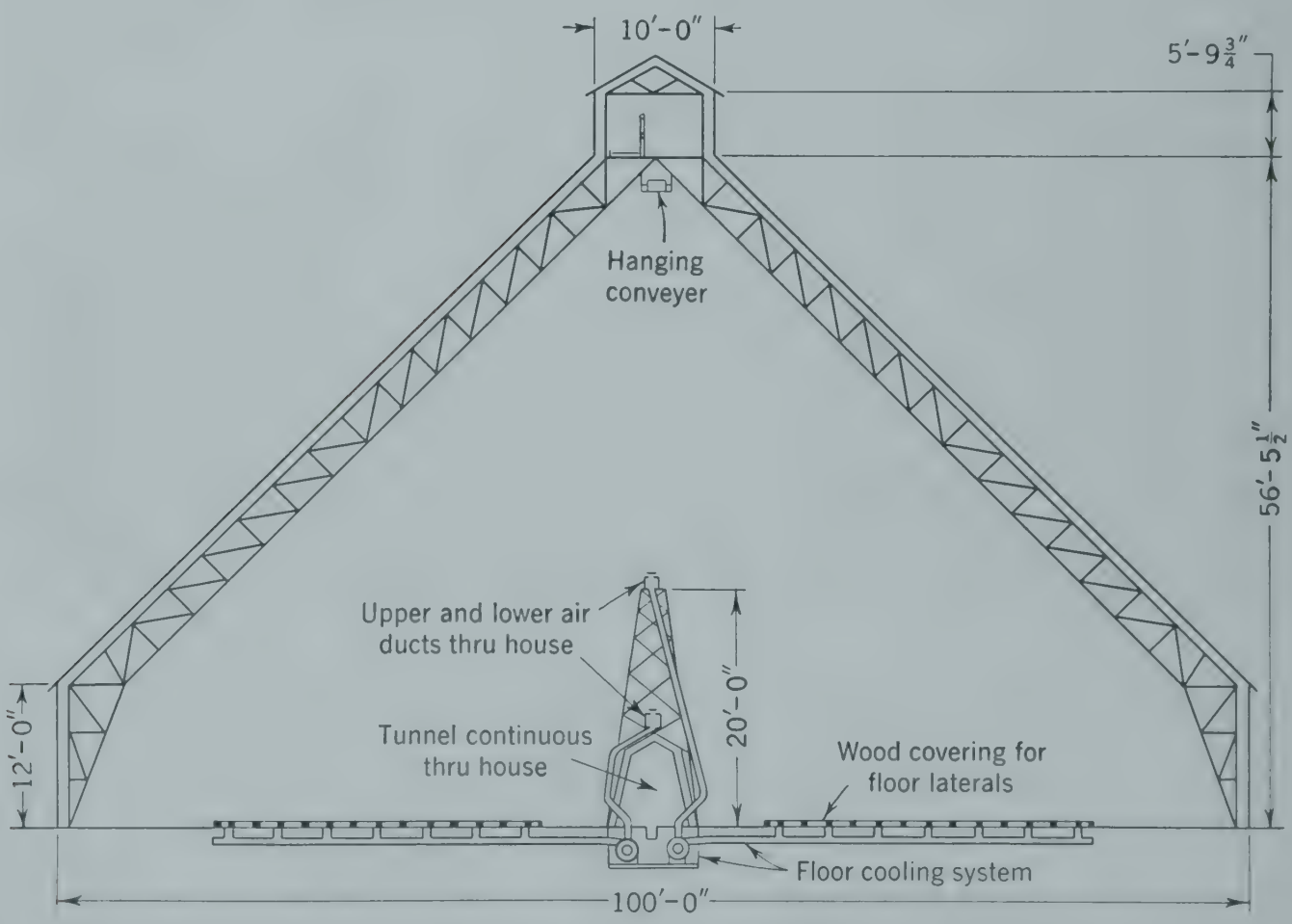


Fig. 126. Cross section of Muskogee-type seed house, showing air-cooling system. (Courtesy *Muskogee Iron Works.*)

The newer seed houses constructed of steel with metal sides and roof have replaced many of the wooden structures. Also, many new units have been built at mills, to increase storage capacity and to furnish storage with adequate seed cooling equipment.

The Muskogee-type seed house, illustrated in Figure 125, is one of the types in common use in the cottonseed industry. These units come in a variety of standard sizes to meet specific storage capacity requirements of the mills. Normally, the storage houses are about 90 to 120 feet wide and from 100 to 200 feet long. The slope of the roof is 45°, which is close to the normal angle of repose of cottonseed. Figure 125 shows the drag elevator to the monitor of the seed house, where the seed are distributed by means of a screw conveyor. It shows also the unloading station and the official 2½-bushel seed sample containers with close-fitting lids, placed under a shelter to protect the cans from direct sunlight and rain.

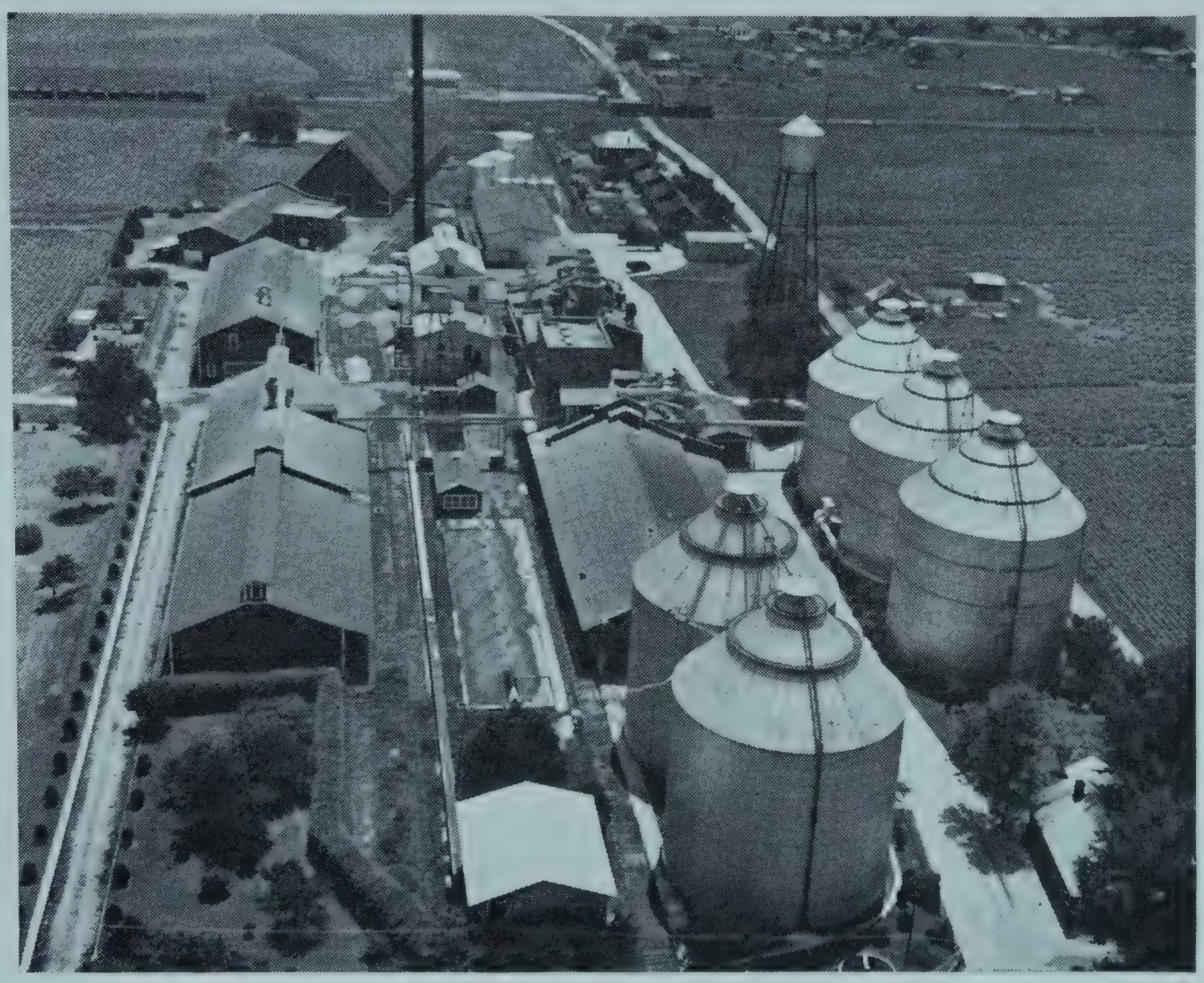


Fig. 127. Aerial view of cottonseed mill, showing silo-type seed storage houses.

Figure 126 shows a cross section of a typical Muskogee house. The indicated truss construction eliminates the damage caused to supporting columns which was experienced in the old seed houses when seed "caved." Lateral seed ventilating ducts located every 8 feet extend along the floor of the house as indicated in the figure. The various lateral air ducts may be shut off from the central pipe, which is connected to a single or double 40- or 60-inch fan. It is possible, therefore, to concentrate the air ventilation or air-cooling on certain sections of the house where warm or hot spots may have developed.

This type of storage unit is generally popular because of its usefulness when the house has been emptied of cottonseed. It can be used with little expense as general warehouse storage space for cottonseed products—slabcake, meal, hulls, or lint—or for equipment when necessary. The silo-type unit does not lend itself well to other storage uses.

B. Silo-Type Storage Units

Silos of various capacities ranging usually from 1,000 to 4,500 tons have been erected for cottonseed storage. Some of the smaller units, 30 to 50 feet in diameter, have been constructed of brick and tile. The larger tanks, which are 70 feet in diameter by about 60 feet high on the straight side, are built of steel. Figure 127 is a photograph of a cotton oil mill with five large steel silos.

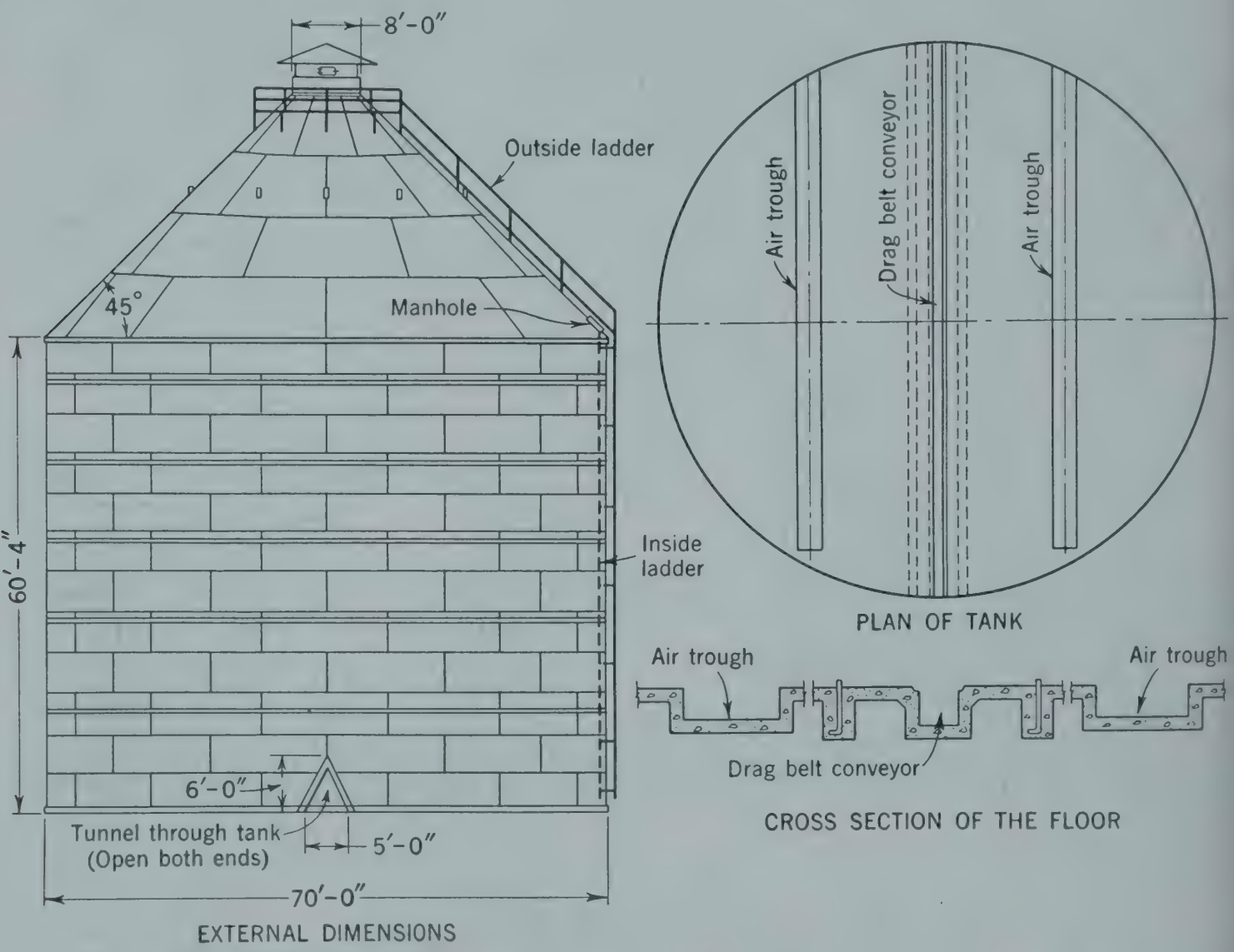


Fig. 128. Silo-type cottonseed storage unit, showing air-cooling ducts.

The seed are conveyed from the unloading station over a perforated conveyor to remove sand and gritty foreign material. The seed pass on to a Roots blower and are blown to the top of the silos through 10-inch pipes. Here the seed are spread by a rotating seed distributor which operates continuously by centrifugal action as the seed are blown into the silo. An electrical device operating a red light indicates to the operator when the seed distributor is not functioning properly. The seed distributor produces a rotating spray of seed over the entire area of the tank. This

results in a blending of seed, which is important from a moisture equilibrium point of view. It also lays down successive, fairly uniform layers of seed as the tank is filled. This is an aid in better air-cooling before the tank is completely filled. Air-blowing the seed to the tanks reduces the moisture content of high-moisture seed and also cools the seed.

Figure 128 shows a cross section of the silo-type storage unit. Normally, a double 60-inch fan is connected to the two main air ducts. The entire floor of the silo has a false bottom, which permits uniform air ventilation.

VI. Control of Deterioration in Storage

A. Air-Cooling of the Stored Seed

The development of air-cooling for cottonseed over a period of years has been the prime factor in controlling deterioration of seed in storage. Air-cooling makes it possible to store prime quality cottonseed in lots of up to 4,000 tons or more for periods of over one year, if desired. Seed in large quantities have actually been stored for periods of more than 1½ years without any untoward developments, with the production of normal yields and prime products throughout.

TABLE 163

Capacity of 40- and 60-Inch Fans

Size	How connected	Main pipe area, sq. ft.	Speed, r.p.m.	Static pressure, in. water	Capacity, cu. ft./min.
Single 40-inch	—	1.4	1300	5	5,090
Double 40-inch	Parallel	1.4	1300	5	10,180
Double 40-inch	Parallel	1.4	1835	10	14,400
Double 40-inch	Series	1.4	1835	18	23,040
Single 60-inch	—	3.14	948	6	12,550
Double 60-inch	Parallel	3.14	866	5	22,900
Double 60-inch	Series	3.14	866	9	36,640

Table 163 shows the capacity of various Buffalo fans used for air-cooling seed in houses or silos.

The development of properly designed seed storage units equipped with adequate air-cooling facilities has been of the greatest importance to the cottonseed milling industry. It permits the existence of a sounder industry with year-round operation instead of rush operation at high capacity for several months and then complete shutdown of the mill with attendant layoff of many workers.

A number of investigators [5] have discussed the cooling of cottonseed

[5] E. L. Tessier, *Cotton Oil Press*, No. 3, 10, 22 (1920). J. E. Roberts, *Cottonseed Oil Mag.*, **46**, No. 7, 17 (1926). T. J. McNulty, *Cotton Oil Press*, **11**, No. 3, 22 (1927).

in storage by blowing air through the seed from the bottom to the top rather than in the usual direction, from top to bottom. This practice, even with the use of air dehumidification equipment, has not proved practical. The air passing through the seed picks up moisture which is often condensed on the cool roof walls and thus virtually "rains" on the seed in the storage unit, causing marked deterioration of the upper layers of seed.

B. Moisture Limits for Stored Seed in Relation to Atmospheric Temperatures

Oil mill operators have developed definite rules, based on experience, for safe storage of cottonseed at different periods of the fall season. This depends on the prevailing and expected normal mean atmospheric temperatures and the type of storage unit and *air-cooling facilities* available.

With adequate and flexible air-cooling equipment connected to storage units, the seed moisture temperature limits are fairly wide. These limits can be further extended if the storage units are not filled to capacity but held at about 50 to 75% of capacity to permit an increased flow of air through the seed. Later in the season, with cooler prevailing atmospheric temperatures, the storage units may be filled to capacity with seed of approximately the same moisture content.

Important items to be considered for safe storage of cottonseed are: (*a*) mean atmospheric temperature and expected temperature based on past records, (*b*) temperature of the seed as unloaded, (*c*) moisture content of the seed, (*d*) free fatty acid content of the seed, and (*e*) size of the air-cooling equipment.

During hot August and early September weather, only low-FFA seed up to about 12.5% moisture content should be stored in large quantities. Later in the season, with cooler weather prevailing (below 70° F. mean temperature) low-FFA seed up to 16% moisture content can be stored with safety.

Low-FFA and low-moisture cottonseed (10–11%) may be stored temporarily in relatively small quantities in nonair-cooled houses or silos without serious deterioration when the mean atmospheric temperature is below 75° F. (see page 584).

C. Control of Seed Temperatures in Storage

After a seed house or silo has been filled, the seed are leveled to obtain more uniform cooling air distribution, and a series of thermometer rods is installed. These are ¾-inch iron pipes with a properly shaped point which are driven into the seed in sections. The pipes are uniformly spaced at distances of about 10 feet and driven to points near the bottom of the seed piles. Normally, three or more metal-sheathed thermometers are attached to a cord and lowered into the pipes at different levels. In large

steel silos, normally 5 to 7 thermometer pipes are installed. In seed houses, the distance between thermometer pipes is about 10 feet.

While seed storage units are being filled during August and September, it is often necessary to know the temperature of the seed in storage. Usually lateral pipes are driven into the seed and sheathed thermometers are inserted in these pipes by means of a wire.

Early in the season the seed thermometers are read daily, in order that the seed may be cooled where necessary. Certain spots in the storage unit may show a considerably higher temperature rise than others and these can be cooled effectively by concentrating the cooling air upon the corresponding sections.

Unless dangerous heating occurs in a storage unit, the seed are air-cooled only during the cooler night hours. It is desirable to bring the average temperature of the seed to below 60° F. as soon as possible. Seed which are to be milled by spring should be cooled to an average temperature of about 50–60° F. Seed to be stored into the summer months should be cooled to about 40° F.

D. Course of Free Fatty Acid Increase in Stored Seed

The biological processes which take place in stored wet seed liberate heat. Due to the insulating effect of the lint on cottonseed, the heat generated is not readily dissipated, hence the mass of seed rises in temperature. Malowan[6] has discussed the changes which take place when cottonseed undergo heating. He has shown that heating can be controlled by air-cooling the seed, but that heating may reoccur unless the moisture content of the seed is reduced sufficiently. Seed which have been through a "heat" and are then air-cooled are reported to show definitely less tendency to further heating.

Altschul[7] has discussed the biological processes in cottonseed and has stated that wet seed as received by the mills are intermediate between dry *dormant* seed and germinating very wet seed. High-moisture seed are wet enough to permit considerable enzyme activity with accompanying gradual digestive breakdown of the oil, carbohydrates, and protein in the kernel. Olcott and Fontaine[8] have shown that the oil content of germinating cottonseed after 139 hours was reduced to half the original amount, and the residual oil in the kernel rose to 20% in free fatty acid content.

The respiratory enzyme action in wet cottonseed proceeds slowly even at temperatures of 50° F. At higher temperatures, the reaction rate is increased markedly as shown in Figures 129 and 130.

[6] J. Malowan, *Cotton Oil Press,* **4,** No. 11, 47–49 (1921); **5,** No. 4, 40–43 (1921).
[7] A. M. Altschul, *Oil Mill Gazetteer,* **49,** No. 1, 8–9, 11, 13 (1944).
[8] H. S. Olcott and T. D. Fontaine, *J. Am. Chem. Soc.,* **63,** 825–827 (1941).

Many investigators [9, 10] have reported the rate of increase in free fatty acids during storage at various seed moisture and seed temperature levels. Freyer [9] and others have published graphs and tables showing the effect of moisture in seed on the rate of free fatty acid rise during storage.

Data on the rate of free fatty acid increase in seed of different qualities stored experimentally under conditions of constant moisture and tempera-

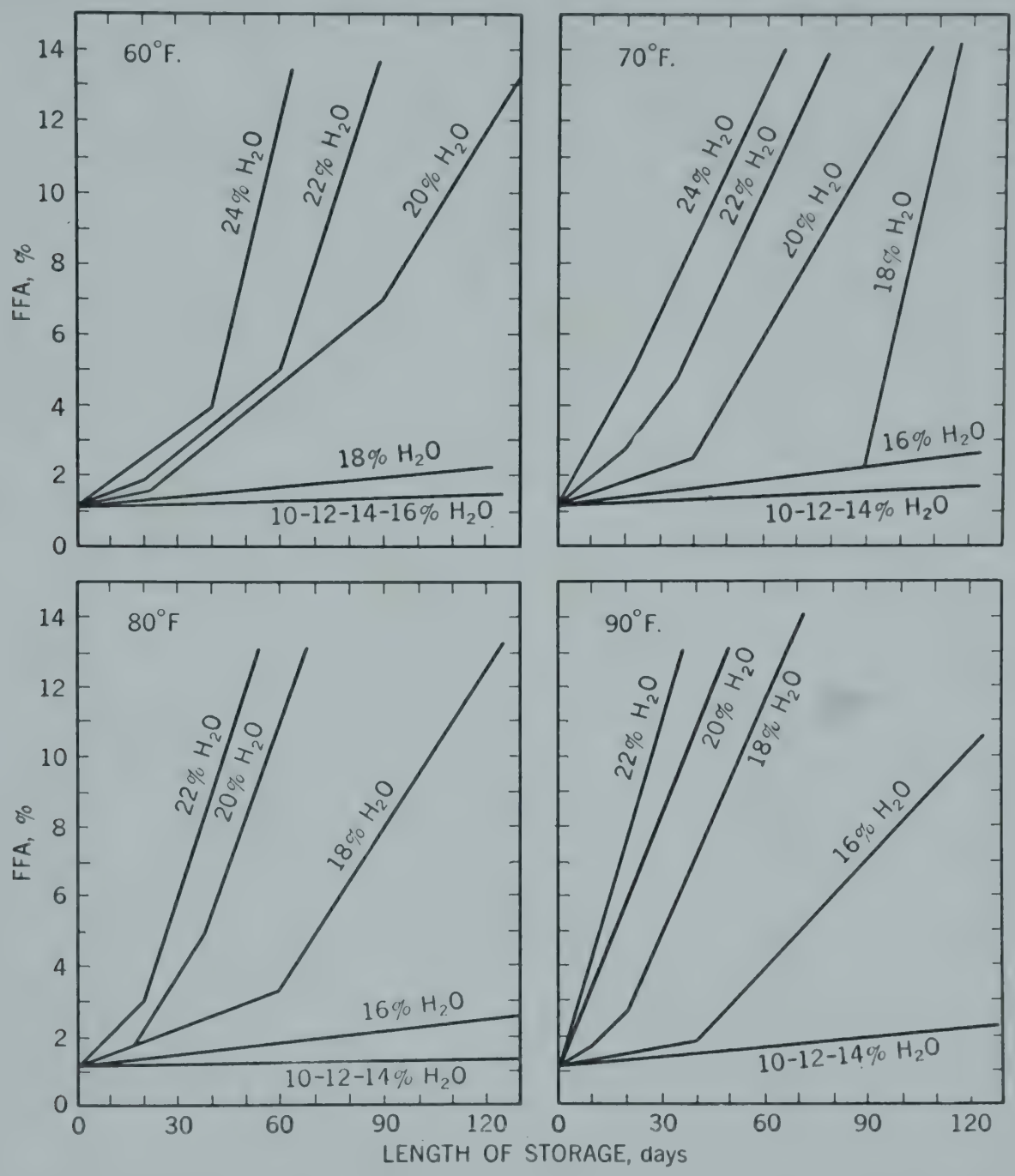


Fig. 129. Free fatty acid increase in prime cottonseed stored at different temperatures and moisture contents.

ture are shown in Figures 129 and 130. Figure 129 shows the rate of rise in free fatty acids of prime cottonseed having an original free fatty acid content of 1.2% and a moisture content varying from 10 to 24%. These seed were stored at constant temperatures of 60°, 70°, 80°, and 90° F. in tight cans, but were removed and mixed in a large can at sampling periods—some

[9] E. Freyer, *Oil & Soap*, **11**, 162–164, 176 (1934).

[10] M. L. Karon and A. M. Altschul, *Plant Physiol.*, **19**, 310–325 (1944). J. Malowan, *J. Oil & Fat Ind.*, **4**, 127–130 (1927). J. B. Rather, *Arkansas Agr. Expt. Sta. Bull.*, **125** (1916). F. R. Robertson and J. G. Campbell, *Oil & Soap*, **10**, 146–147 (1933). D. M. Simpson, *J. Agr. Research*, **50**, 449–456 (1936). M. K. Thornton, Jr., and P. P. Briggs, *Oil Mill Gazetteer*, **33**, 15 (Dec., 1929).

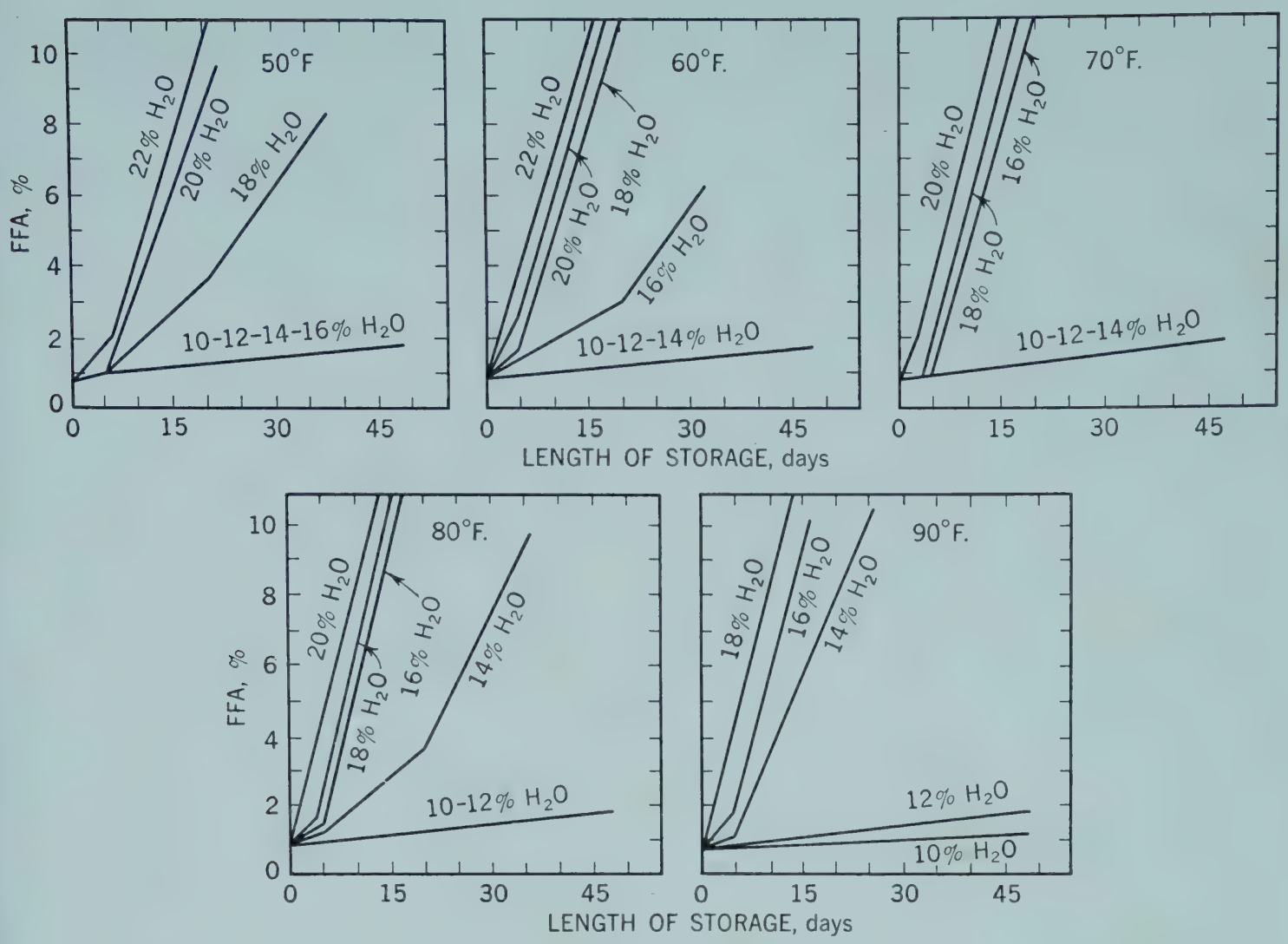


Fig. 130. Free fatty acid increase in slightly damaged cottonseed stored at different temperature and moisture levels.

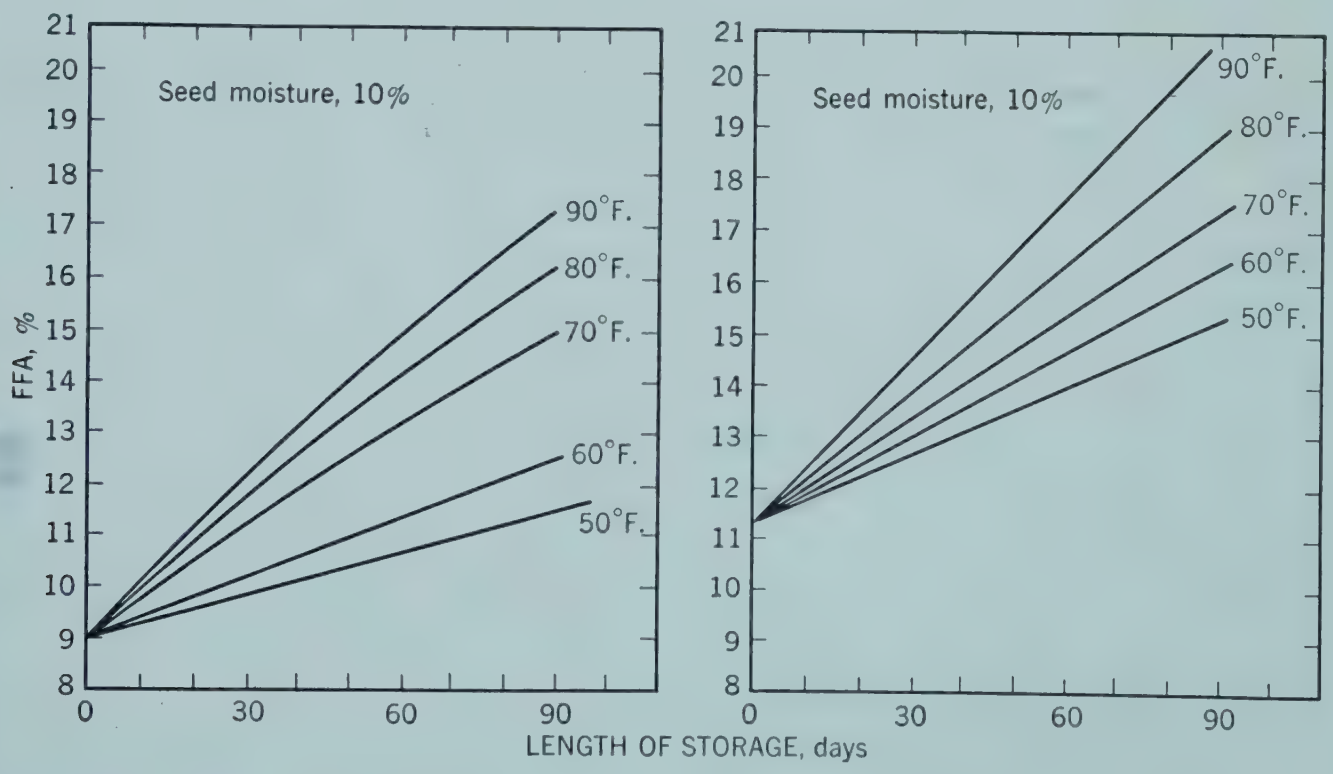


Fig. 131. Free fatty acid increase in cottonseed, initially high in free fatty acids and containing 10% moisture, upon storage at different temperatures.

drying occurring during mixing. The seed averaged about 2–3% lower in moisture content than indicated in the figure, after 4 months' storage and repeated sampling. The effect of temperature and moisture on rate of rise is marked. Under the conditions of storage indicated, prime seed of up to 14%

moisture content can be stored with relative safety. At 60° F., prime seed of up to 16–18% moisture content can be stored with the expectation of a relatively low rise in free fatty acids.

Figure 130 shows similar storage results for 0.8% FFA seed in which about 10% of the kernels were damaged. Seed of this quality show a much higher rate of deterioration in storage. It is possible to store safely seed of this quality even at 90° F., provided the seed moisture is not above 12%.

Figure 131 shows the rapid rise in free acids when 10% moisture, high-FFA cottonseed are stored in air-tight cans at 50° to 90° F. The rate of deterioration is so rapid that seed of this quality should be stored only in case of emergency. About 10% of the seed in this lot were damaged (*i.e.*, contained off-colored meats).

E. Typical Air-Cooling Results in Mill Storage

The actual deterioration of seed in storage is somewhat less than indicated by Figure 129, due to the drying of the seed with air-cooling. During storage, air will be drawn through the seed for long periods, varying from 200 to 700 fan-hours. The time required to cool the seed depends on the moisture content, atmospheric temperature, and the time of the year when the seed will be processed.

Typical results obtained in normal large-scale storage are shown in the accompanying table.

Seed moisture, %	FFA content before storage, %	Average seed temperature, °F.	Rise in FFA content per month in storage, %
10–11	1.0	50	Less than 0.1
10–11	2.5	50	About 0.2
10–11	5.0	50	About 0.5

F. Storage of High-FFA Seed

Cottonseed above 2.5% in free fatty acids deteriorate much more rapidly than seed with 1% free acids. The rate of deterioration is accelerated decidedly with increase in the moisture content.

High-FFA seed should be sent directly to the mill whenever possible to prevent fast deterioration in storage, as indicated by Figure 131. (The seed were stored in tightly sealed friction-top cans at the temperatures indicated.) When large quantities of high-FFA seed are received at mills as the result of extended bad storms over large areas, it is necessary to store the seed temporarily. The following precautions should be closely observed:

(*a*) Store in small units equipped with the best air-cooling facilities. Cool to 60° F. or less as soon as possible. Watch seed temperatures in storage daily.

(*b*) Seed moisture is very important. Segregate all low-moisture seed stored. Dry all high-moisture seed to 10% moisture content, if dryer is available; otherwise, mill directly.

(*c*) Store seed by FFA brackets, *viz.*, 2.5 to 5.0%, 5.0 to 8.0%, 8 to 10%, etc.

(*d*) Mill highest temperature seed first, if it contains hot spots or is above 70° F. average temperature; otherwise, mill highest FFA seed first.

With close control and adequate air-cooling, it is possible to store seed containing 2.5 to 5.0% free acids and 10 to 11% moisture in lots of about 2,500 tons. There is about a 0.5% increase in the free fatty acids per month of storage, provided the average seed temperature is reduced to 60° F. or lower.

One cannot stress too much the need for extreme watchfulness when storing high-FFA seed above 10% moisture content. These seed will heat in pockets and seed temperatures must be read daily in order to air-cool selectively. Unless these seed are watched daily, the entire seed mass may char.

G. Chemical Treatment to Inhibit Deterioration

Altschul and colleagues [11, 12] have reported that treatment of high-moisture cottonseed with ammonia is effective in reducing deterioration. Laboratory and semipilot plant tests showed a marked reduction in free fatty acid increase in cottonseed of 15% moisture content stored for periods of 5 to 6 months when the seed was treated with ammonia. However, ammonia treatment of cottonseed was not very effective once the seed had developed considerable lipolytic activity, *i.e.*, after the seed had already developed a considerable free fatty acid content.

The authors indicate that about 10 pounds of gaseous ammonia or 30 pounds of aqua ammonia is adequate per ton of seed to bring the *p*H of a water extract to about 8.0, which is a satisfactory level. The ammonia can be added by spraying the seed in a conveyor with aqua ammonia. The use of ammonia also results in lightening the color of the oil.[12]

More recent work [13] shows that plant-scale tests have not been satisfactory using ammonia. However, the vapors from a commercial preparation of sodium alkyl aryl sulfonate, when drawn through seed containing 13.5% moisture and 7.3% free fatty acids, was found to be an effective inhibitor of heating and free acid development during a five months' storage period.

[11] A. M. Altschul, M. L. Karon, L. Kyame, and M. Caravella, *Oil & Soap,* **20,** 258–262 (1943). A. M. Altschul, *Oil Mill Gazetteer,* **49,** No. 1, 8–9, 11, 13 (1944).

[12] A. M. Altschul and M. L. Karon (to the Secretary of Agriculture), U.S. Pat. 2,376,852 (1945).

[13] A. M. Altschul, M. E. Curet, M. L. Karon, C. Hall, and B. A. Smith, *Oil Mill Gazetteer,* **50,** No. 8, 9 (1946).

CHAPTER XIV

MECHANICAL PRETREATMENT OF THE SEED[1]

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College Station, Texas

I. Cleaning of Cottonseed[2]

Cottonseed as fed to the mill are contaminated with varying amounts of foreign matter, such as pieces of boll hull, locks of cotton, rocks, sand, earth, twigs, leaves, nails, bolts, other bits of metal, pieces of wood, etc., all of which must be removed. Unless some of this foreign matter is removed, the operation of machines for subsequent processing is almost impossible, since it is capable of causing damage so severe as to render the machines inoperable. Another very important reason for cleaning the seed is to improve the quality of the finished products, especially linters. While linters may be cleaned to good advantage after removal from the seed, lint cleaning is not in any sense a substitute for seed cleaning. There are certain items of operating cost that are directly affected by the quality of the cleaning done, for example, file and gummer cost, linter saw cost, general maintenance throughout the plant, labor for sweeping, and even press cloth cost in hydraulic mills. Furthermore, the improvement in working conditions and the reduction in fire hazards that go with better seed cleaning are not to be overlooked.

[1] General References: A. E. Bailey, *Industrial Oil and Fat Products,* Interscience, New York, 1945; L. L. Lamborn, *Cottonseed Products,* Van Nostrand, New York, 1920; C. L. Lockett, *Cotton and Cotton Oil Press,* **42,** A-3 (April 12, 1941) and **45,** A-3 (July 15, 1944); M. K. Thornton, Jr., *Cottonseed Products,* Oil Mill Gazetteer, Wharton, Texas, 1932; W. R. Woolrich and E. L. Carpenter, *Mechanical Processing of Cottonseed,* Eng. Expt. Sta., Univ. Tenn., Knoxville, 1935.

[2] For further information on the various phases of cottonseed cleaning, see the following: E. Bradshaw, *Oil Mill Gazetteer,* **36,** 17–20 (Feb., 1932); E. L. Carpenter, *Cotton and Cotton Oil Press,* **34,** 3–4 (Nov. 4, 1933) and **34,** 5 (Nov. 11, 1933); F. A. Collins, *Oil Mill Gazetteer,* **33,** 9 (Oct., 1929); J. P. Dickinson, *ibid.,* **34,** 9 (Aug., 1929); J. P. Greenwood, *Cotton Oil Press,* **12,** 35–38 (Aug., 1928); C. L. Lockett, *Oil Mill Gazetteer,* **34,** 13 (June, 1930), *Cotton and Cotton Oil Press,* **39,** 10 (Nov. 12, 1938), and *Cotton Oil Press,* **10,** 29–30 (July, 1926); E. C. O'Neill, *Oil Mill Gazetteer,* **39,** 11, 13, 15 (Sept., 1934); C. B. Richardson, *Cotton Oil Press,* **10,** 32–33 (March, 1927); C. L. Stacey, *Oil Mill Gazetteer,* **44,** 36–37 (July, 1939); J. J. Thiessen, *Cottonseed Oil Magazine,* **39,** 11 (1923).

A. Reels

Probably one of the earliest seed cleaning devices and one which is almost indispensable today in handling certain types of cottonseed is the boll reel, Figure 132. It is an inclined revolving screen of cylindrical or hexagonal cross section with perforations sufficiently large to allow seed and foreign particles of equivalent size to fall through, while foreign matter of greater bulk is discharged at the further and lower end. Some mills do not use boll reels, while others claim that they could not afford to operate without them when working seed which contain large amounts of coarse foreign matter, especially loose locks of cotton. Of the loose cotton that

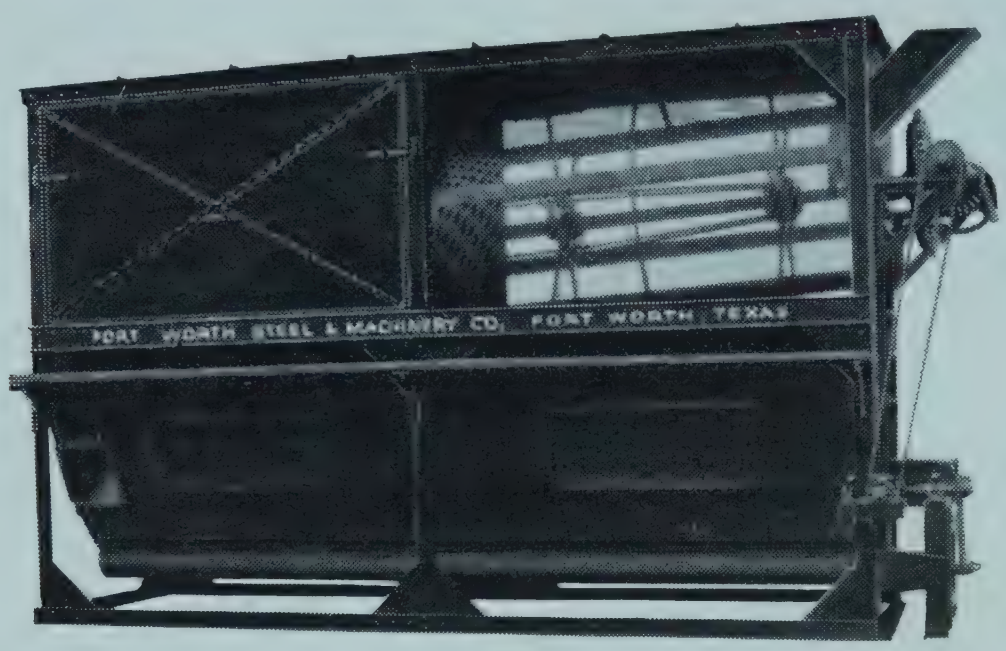


Fig. 132. Boll reel for cleaning of cottonseed. (Courtesy *Fort Worth Steel & Machinery Co.*)

occurs in cottonseed, a larger portion tends to stick in the screens on almost any other type of screening device. In the boll reel, this stubborn foreign matter falls out of its lodging place when the screeen in which it is lodged reaches the top position in the revolution of the reel. It is also possible to install continuous brushing equipment to assist in the cleaning operation, provided the reel is cylindrical in cross section. Cylindrical reels have the advantage of being easily cleaned in operation, while hexagonal reels have to be stopped for cleaning.

For best results, a boll reel should be covered with ½-inch round perforated metal over the entire length, however, 4 to 6 feet of ⅝-inch metal on the discharge end will give good results. A 60-inch diameter round reel, 18 feet long, inclined ½ to ¾ inch per foot of length, clothed with ½-inch metal, will handle 75 to 100 tons of cottonseed per 24 hours, if the seed are not excessively trashy or woolly, the reel is operated at the proper speed, and the feed is uniform. The proper speed and uniformity of feed are both extremely important to the successful operation of a reel. A reel should revolve at a speed slow enough that its load is not held to

the metal by centrifugal force, yet fast enough to throw the seed over the shaft passing through the center of the reel. The correct speed for a 60-inch diameter reel is about 17 r.p.m. The feed should be controlled by a mechanical feeder with considerable volume in the hopper over the feeder to take care of any shock in load. The power requirement for a 60-inch diameter boll reel, 18 feet long, should not exceed 5 h.p.[3] if properly operated.

Sand reels have been in use about as long as boll reels. The construction of the sand reel is very similar to that of the boll reel. In operation, sand and other fine foreign matter falls through the openings in the perforated metal and the seed discharges from the end of the reel. Sand and boll reels when used together are usually mounted in the same frame one above the other. While sand reels give the seed a beating action that is good for loosening up dirt, the use of sand reels is not considered to be absolutely necessary when sufficient capacity in reciprocating screens for sanding is available.

B. Pneumatic-Mechanical Screens

The most effective seed cleaners in use are those which employ both shakers and the pneumatic principle. While machines of various manufacturers are different in the size, number, and location of shakers and in details of construction of the pneumatic separators, the machine shown in Figure 133 is typical of this type of cleaner and will serve to illustrate the principle involved. This machine is built and functions approximately as follows:

(*a*) An air current contacts the seed as it is discharged from the feeder to the upper tray, thus minimizing the tendency to create a dust-laden atmosphere in the cleaning room.

(*b*) The upper tray with $\frac{5}{8}$-inch diameter (maximum) perforations removes broken bolls and other coarse alien matter, and delivers the seed to the upper end of the lower tray.

(*c*) The lower tray preferably should have at least the first six feet with $\frac{1}{8} \times 2$-inch herringbone-type perforations to remove sand, small twigs, etc.; the remaining maximum of four feet should have $\frac{1}{4}$-inch diameter perforations to separate the black seed, which pass directly to the stoner for aspiration and separation of small stones, etc.

(*d*) Screened seed from the lower tray are delivered directly to the aspiration chamber, where they immediately come into contact with a vertical air stream which has sufficient velocity to carry the woolly seed while permitting black seed, stones, metals, and other heavy alien matter to drop to an internal conveyor for delivery to the stoner for final purification.

(*e*) Gray seed are deflected horizontally against a baffle of woven wire screen with sufficient impact to loosen the fine sand and dust usually embedded in the

[3] H. E. Ayres, *Oil Mill Gazetteer,* **45,** 32–35 (Aug., 1940).

mat of short fibers. This also has the effect of jarring loose shale and boll particles which otherwise would cling to and continue with the seed. The material which passes through the screen is discharged through a conveyor on the rear of the chamber; the remainder is picked up by the fan and blown to a dust room or to a cyclone collector with an internal displacement of approximately 100 cu. ft.

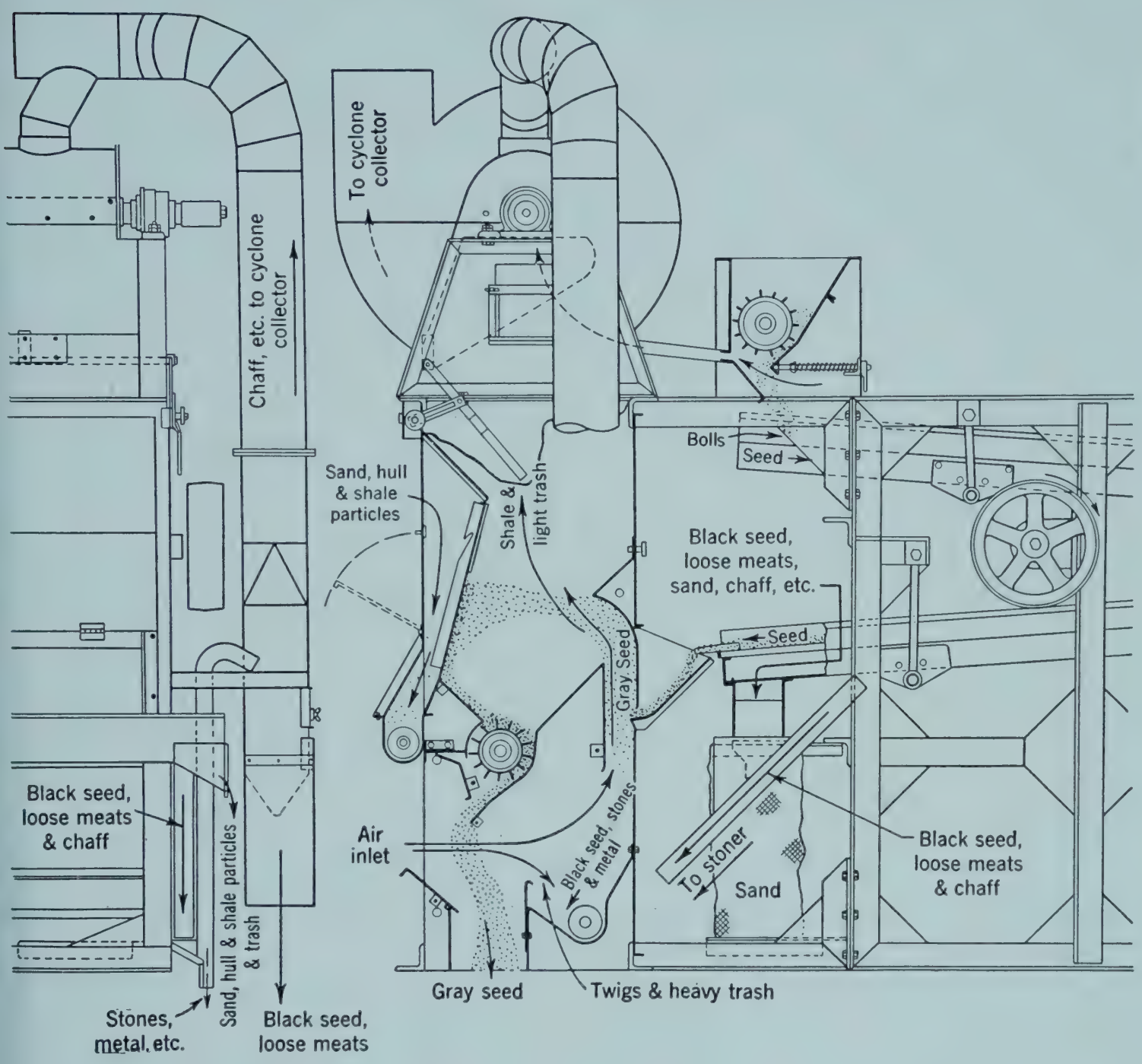


Fig. 133. Pneumatic-mechanical cottonseed cleaning unit. (Courtesy *The Bauer Bros. Co.*)

(*f*) Final treatment occurs as the seed falls in a vertical sheet from the discharge roll to a cleaned seed conveyor where it comes into contact with a horizontally flowing air current which deflects small foreign particles lighter than the seed, depositing these in an internal conveyor.

Shaker speeds are very important. The proper speed for one shaker may not be correct for another. The speed recommended by the manufacturer is usually very close to being right. However, if the shaker has been subjected to any changes that have altered the pitch of the shaker, the type or setting of the hangers, or the throw of the eccentric, the manufacturers standard speed rating will not necessarily be correct. Shakers

with a flat pitch and long throw eccentrics operate better at lower speeds than do shakers with a steep pitch and short throw eccentrics and *vice versa*. The eccentric shaft on the cleaner described in Figure 133 should run at 300 to 325 r.p.m. The fan should be operated at a speed just sufficient to lift the gray seed and drop the black seed when handling the heaviest class of seed expected. The correct fan speed for the cleaner shown in Figure 133 will be found to be about 1,000 to 1,200 r.p.m. The maximum power requirements for this type of cleaner when operating at the recommended speeds is about 10 h.p. for the 48-inch size. The capacity of the machine described is given by the manufacturer as 120 tons per 24 hours, which is the maximum. Very superior results will be obtained if the machine is operated at 50% of this rating.

C. Rock and Shale Traps

There are several pneumatic cottonseed cleaners that can be very easily installed in a conveyor line by simply removing one section of the conveyor box and placing the cleaner in its place. This variety of cleaner is commonly referred to as the "rock and shale trap type" and, while it is quite worthwhile as an auxiliary or safety device to be used in addition to the regular cleaning setup, it cannot be expected to substitute entirely for the larger and more complicated equipment. These machines are usually so constructed that seed cannot pass beyond the point in the conveyor where the cleaner is located if the machine is not functioning.

D. Magnets

The use of either electromagnets and permanent magnets at various points through the plant and especially ahead of each individual linter is common and good practice.

II. Humidification of Cottonseed

The advantage of working cottonseed containing the optimum moisture content has long been recognized especially in connection with the proper cooking of the cottonseed meats, however, it is doubtful that there has been general appreciation of the advantages of having the seed at an optimum moisture content for other processing operations. Most attempts to add moisture to dry cottonseed have met with only limited success or outright failure, probably because in most cases the dry condition of the seed has been considered temporary. There seems to be no standard equipment or process in general use in the industry for humidifying cottonseed. Several methods have been tried which have been described in the literature on humidifying.[4] Some good points to observe in connection with the

[4] C. C. Castillow, *Oil Mill Gazetteer,* **44,** 37–38 (July, 1939). J. P. Dickinson, *ibid.,* **43,** 11–12 (Dec., 1938). H. C. Graebe (to Procter & Gamble Co.), U.S. Pat. 1,707,949 (1925). M. K. Thornton, Jr., *Oil Mill Gazetteer,* **42,** 11 (June, 1938). A. C.

humidification of cottonseed are as follows: (*a*) The moisture or water added should be in a finely divided state and as uniformly distributed as possible. (*b*) The time of contact between moisture and seed should be as long as is practicable. Three or four days time is not too long if the seed are free from loose meats. (*c*) Surface moisture is quite objectionable from a handling and processing standpoint. (*d*) Moist cottonseed will deteriorate faster than dry seed.

III. Delinting

The removal of the short staple lint adhering to the seed after ginning can be accomplished by several different methods.[5] A very popular method used extensively in the preparation of delinted planting seed uses sulfuric acid as a chemical delinting agent. There are other chemical methods which have been tried,[6] however, insofar as the author is aware, none are in use on a commercial scale for any purpose other than the preparation of delinted planting seed. There are several different mechanical methods of delinting cottonseed, some of which have at various times been in operation on a commercial scale. The one method that is almost universally used for delinting cotton is that which makes use of a machine known as a linter. A detailed description of this process follows.

A. The Linter

The cottonseed linter is a machine designed to remove the short staple lint adhering to the seed after ginning. The product produced is known as "cotton linters." Usually the seed is passed through one battery of machines to partially delint the seed and then passed through a second battery to obtain a lint of shorter staple. A typical modern linter installation is illustrated in Figure 134. The amount of lint removed depends on existing markets for the two products known as "first-cut" and "second-cut" linters. Under certain conditions, a single over-all delinting, produc-

Wamble, *ibid.*, **49,** 24–28 (Sept., 1944) and *Cotton and Cotton Oil Press,* **45,** A-3, A-4, A-6 (Sept. 23, 1944). See also J. E. Roberts, *Cotton Oil Press,* **12,** 33–34 (Sept., 1928).

[5] See also the following references covering various phases of delinting: R. E. Cook, *Oil Mill Gazetteer,* **43,** 8 (Aug., 1938); H. F. Crossno, *ibid.,* **42,** 17 (May, 1938); M. C. Dimpful, *ibid.,* **38,** 19–22 (Nov., 1933); R. T. Doughtie, Jr., *ibid.,* **45,** 36–38 (July, 1941); J. P. Greenwood, *Cotton Oil Press,* **12,** 27–29 (Sept., 1928) and **12,** 19 (Oct., 1928); H. Hildebrand, *ibid.,* **11,** 91–94 (June, 1927); C. H. Lickle, *ibid.,* **16,** 9–10 (Sept., 1932); C. S. McKinley, *Oil Mill Gazetteer,* **34,** 13 (July, 1925), **35,** 3 (Sept., 1930), and *Oil Miller & Cotton Ginner,* **36,** 18–19 (Aug., 1930); C. Rankin, *Oil Mill Gazetteer,* **40,** 22–25 (June, 1936); T. L. Rettger, *J. Oil & Fat Ind.,* **3,** 135 (1926); M. C. Verdery, *Oil Mill Gazetteer,* **38,** 13 (July, 1933), **39,** 13–15 (Oct., 1934), **41,** 7 (July, 1936), and *Cotton and Cotton Oil News,* **34,** 3–4 (March 11, 1933); T. P. Wallace, *Oil Mill Gazetteer,* **47,** 3 (Oct., 1942); G. C. Walsh, *ibid.,* **37,** 9–13 (Oct., 1932); R. L. Wickes, *ibid.,* **43,** 7–8 (Aug., 1938).

[6] R. G. Archibald, *Soil Sci.,* **23,** 1–4 (1927). B. T. Ardashev, *Ind. Eng. Chem.,* **25,** 575–581 (1933). A. H. Brown, *Botan. Gaz.,* **94,** 755–770 (1933). C. D. Sherbakoff, *Phytopathology,* **17,** 189–193 (1927).

ing a product known as "mill-run" linters is desirable. The term "linters" is confusing, since both the machine and product are known by this term, so that the product is usually referred to simply as "lint."

The capacity of a linter depends on the amount of lint on the seed as received from the gin and also on the amount of lint to be removed. Except for extremely light or extremely heavy cuts, the capacity of a 141-saw linter may be considered to be approximately 1,000 to 1,500 pounds of lint per 24 hours. The power requirements are approximately 1 h.p. per 100 pounds of lint per 24 hours under normal conditions of operation. The amount of lint on the original seed depends on the variety of the seed

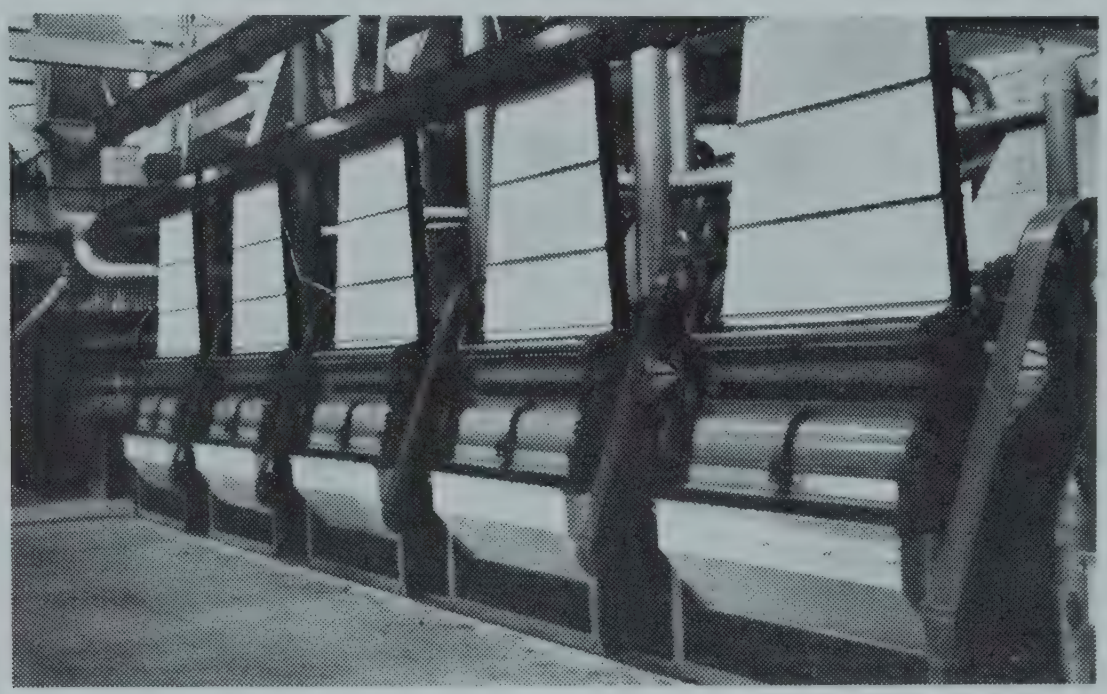


Fig. 134. Typical modern installation for delinting cottonseed. (Courtesy *Carver Cotton Gin Co.*)

and the ginning methods. It may range from 8 to 14%. In some countries, where a large percentage of the seed is bald, it may run even less.

The completeness of delinting desired depends on existing markets. It is now common practice to reduce the lint left on the seed to below 2% and in some cases to below 1%. The capacity of the machine is greatly reduced in obtaining the last traces of lint, and it is only when markets are very favorable that lint is removed to the extent of less than 2%.

The linter is basically similar to a cotton gin using the Eli Whitney saw and rib principle. The saws are more closely spaced than are those of the gin and it is necessary to revolve the roll of seed by power to expose it properly to the saws. Because of the shortness of the lint to be removed, the linter requires greater refinement in its construction than the gin, and greater rigidity due to the higher pressures carried in the seed roll.

A cross section of a linter is shown in Figure 135. The feeder is kept constantly filled with seed from a flared chute which acts as a reservoir and is continuously supplied by an overhead screw conveyor. A corrugated sectional roll turned by means of a ratchet operating from a continuously

running eccentric feeds the seed into the roll of the linter. Between the feeder and the roll the seed slide over a magnet to remove tramp iron. This is preferably of the permanent type made of one of the new permanent magnet alloys.

The seed roll is revolved by a winged shaft called a float in a direction opposite to the saws and at a lower peripheral speed than the saws. The seed roll is confined between a curved metal member called the seed board and the ribs of the "gratefall." The saws project through these ribs and

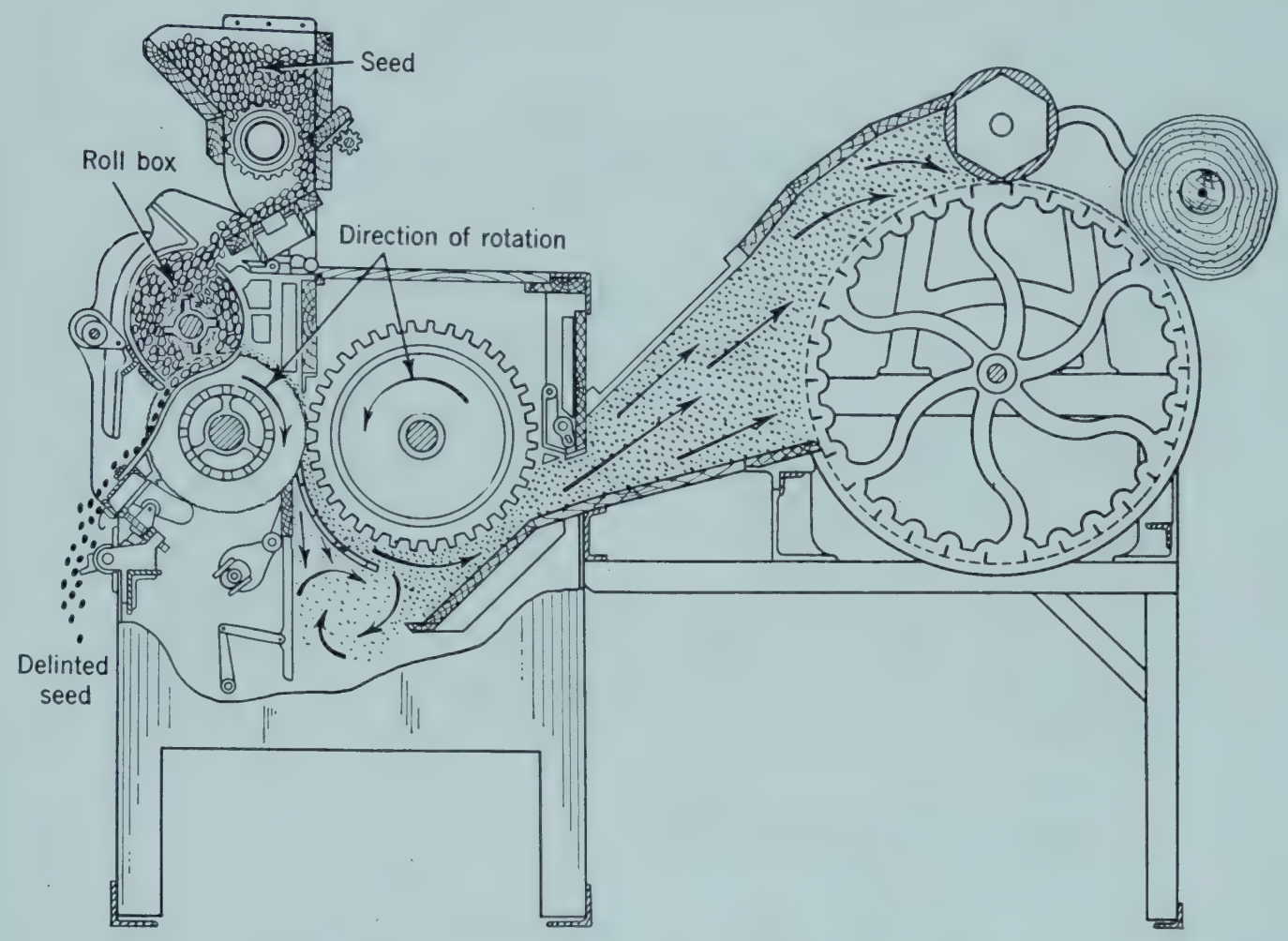


Fig. 135. Cross section of a cottonseed linter.
(Courtesy *Carver Cotton Gin Co.*)

cut through the seed roll, carrying the lint fibers between the ribs, which are set close enough together so that the seed cannot pass through. The bottom of the seed board is adjustable toward the ribs. Rake teeth located at this point extend between the saws, and the size of the opening set between these teeth and the ribs determines the extent to which the seed will be delinted before they drop out of the linter.

As the delinted seed fall out of the seed board, the weighted curved member riding on the roll drops. This curved piece is connected to a shield on the feed roll ratchet, so that as it falls more teeth are engaged and seed are fed into the roll until the latter is again built up. In actual operation, this sequence is smoothed out and the feed is continuously controlled by the amount of seed discharged from the linter.

The lint carried through the ribs is removed by a cylindrical brush

revolving with the saws and at a somewhat higher speed than the saws. This brush is sealed off at the front by the "division board" and at the rear by the "back lip board," so that it also acts as an air pump. The mixture of lint and air carried by its pumping action is slowed down after leaving the ribs by entering an expanded area, and here an eddy current is formed which allows any heavy particles in the lint to drop out. This separation of heavy material is known as "moting," and occurs between the front adjustable baffle, or "air shield" and the rear inclined baffle, or "mote board."

The lint passing over the mote board enters a flue and is blown on a slowly revolving screen or condenser. The screen allows the air to pass through, and the sheet of lint built up on the condenser is rolled up on a roll as a bat. For second-cut and mill-run linters these individual condensers have been largely replaced by a common pneumatic lint flue collecting system. This results in a cleaner lint room and a saving in labor, although additional power amounting to approximately 1 h.p. per linter, in the case of a well-designed system, is required for the flue system. Generally, individual condensers are still used for first-cut linters. A successful dust collecting system has been applied to these individual condensers.

Linters were built for a great many years with 106 saws, but in recent years this has been increased to 141 and now to 176 saws, with a substantial increase in lint yield. The possible increase in the number of saws is limited by the width of the ribs between the saws. These saws are mounted on a shaft and are accurately spaced to correspond to the slots between the ribs in the gratefall. The point where the saw teeth pass down through the ribs is known as the "ginning point" and is subject to the most wear. The gratefall is adjustable at the top and bottom, so that the position of the ginning point can be maintained as the diameter of the saw is reduced by sharpening. This also keeps the proper amount of saw projecting through the ribs.

As the saws are reduced in diameter, it is also necessary to adjust the relation of the saws and brush. In the newer models, the saw cylinder can be adjusted to the brush, but in most of the linters now operating, it is necessary to adjust the brush to the cylinder. In the latter case, the division board and back board must follow the brush. The brush also wears and is occasionally trimmed, so that it is necessary to make it adjustable to the saw in all cases.

The moting of the linter can be adjusted by the draft shield. If this does not give the desired results, a change in the speed of the brush or the individual condenser will usually produce the proper flow of air through the linter.

All these adjustments and other minor ones are purely operational

details, but are very necessary in order to obtain good quality lint and efficient operation.

B. Linter Saw Sharpening Machinery

The cutting of lint is accomplished essentially by the action of the saw teeth on the seed. For this reason, the most vital part of the linting operation is to maintain sharp teeth of the proper shape on the saws. The sharpening of several thousand of these saws daily represents quite a mechanical problem and only the best possible equipment for this operation is economical.

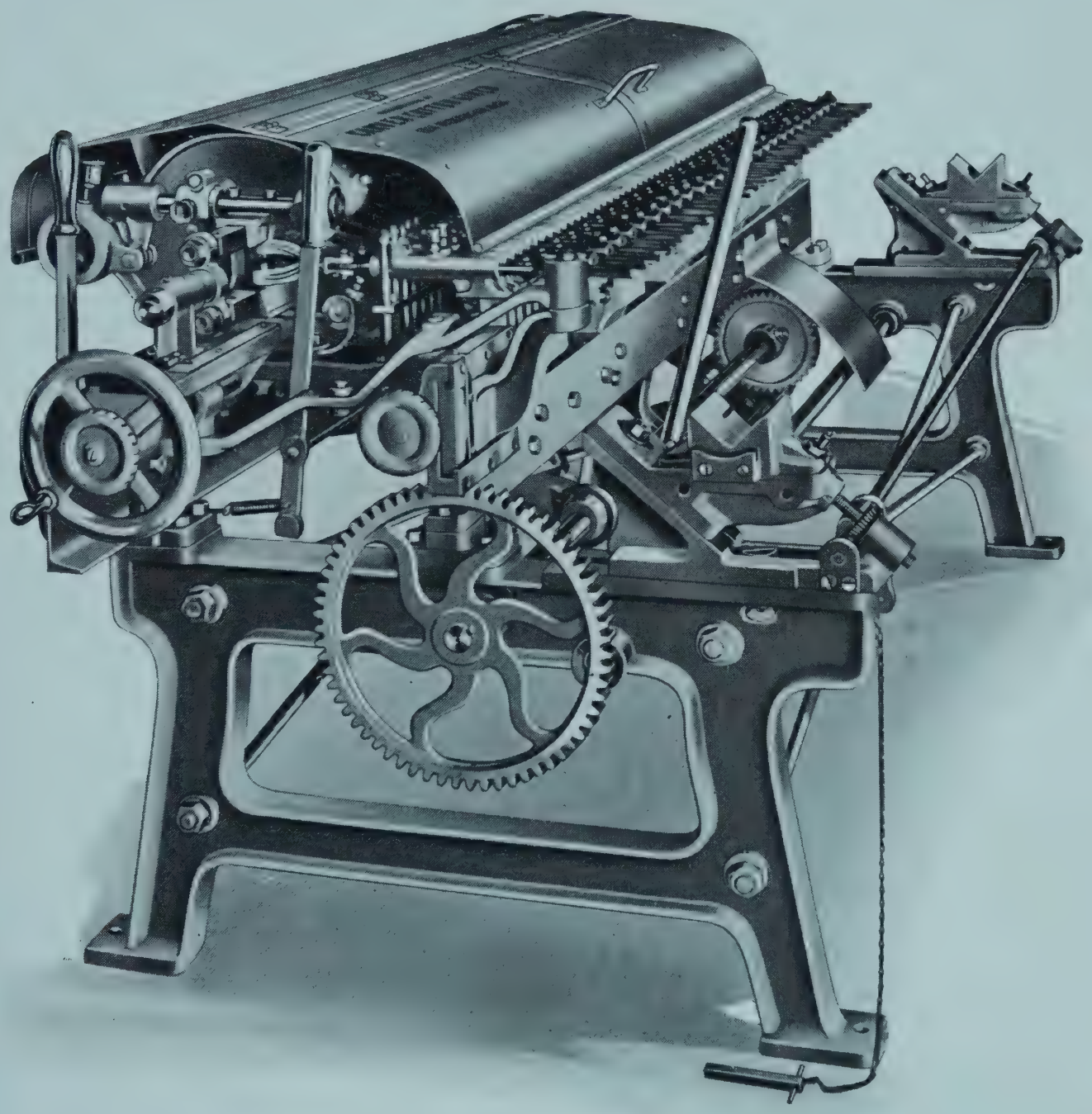


Fig. 136. Modern filing machine for linter saws.
(Courtesy *Carver Cotton Gin Co.*)

Saw sharpening usually consists of two operations. A filing operation on the sides of the teeth with a reciprocating triangular or flat file keeps the teeth pointed. Filing with a rotary file between the teeth—called "gumming"—maintains the length and shape of the teeth. This latter operation is sometimes accomplished with a milling cutter.

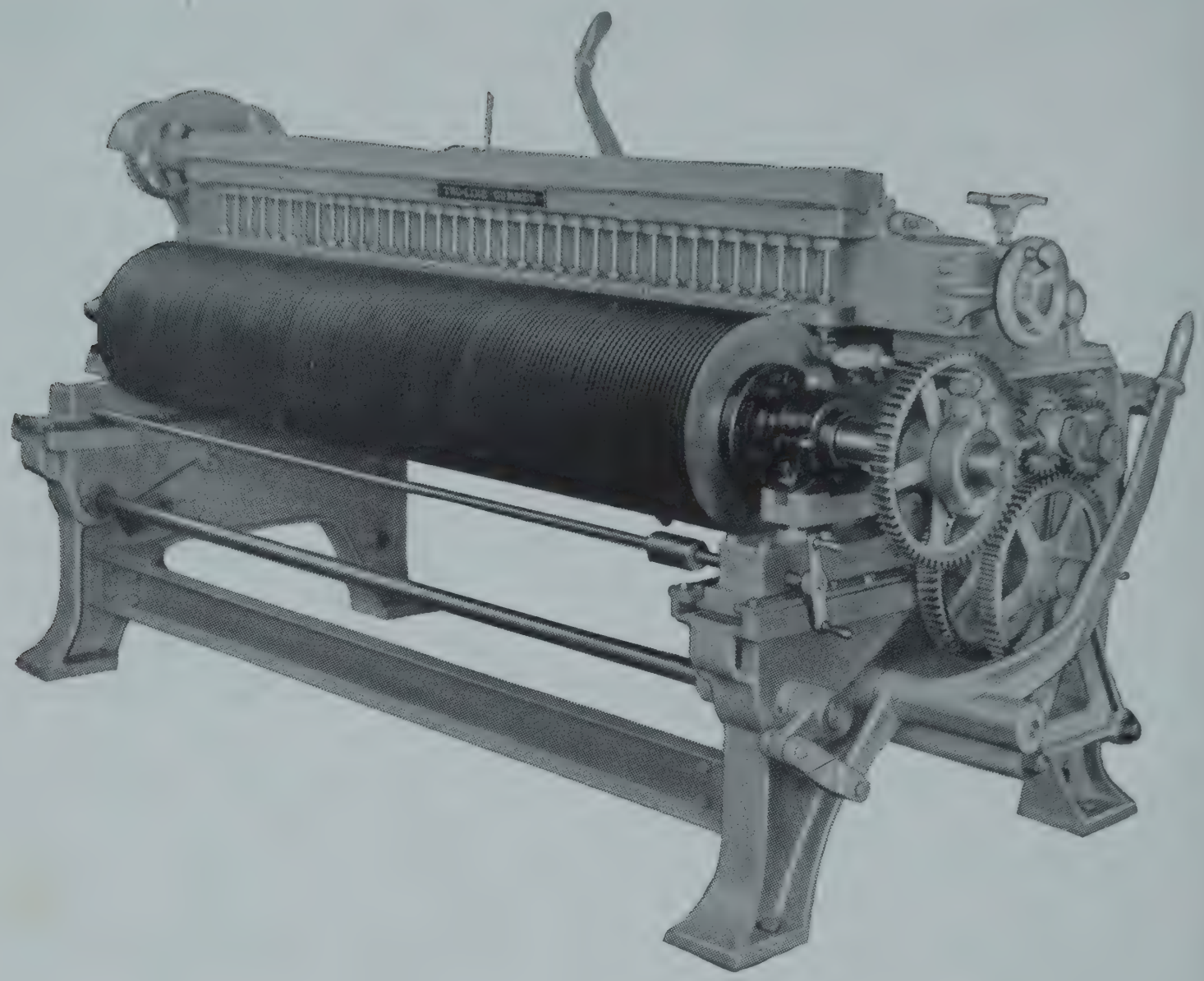


Fig. 137. Modern gumming machine for linter saws.
(Courtesy *Carver Cotton Gin Co.*)

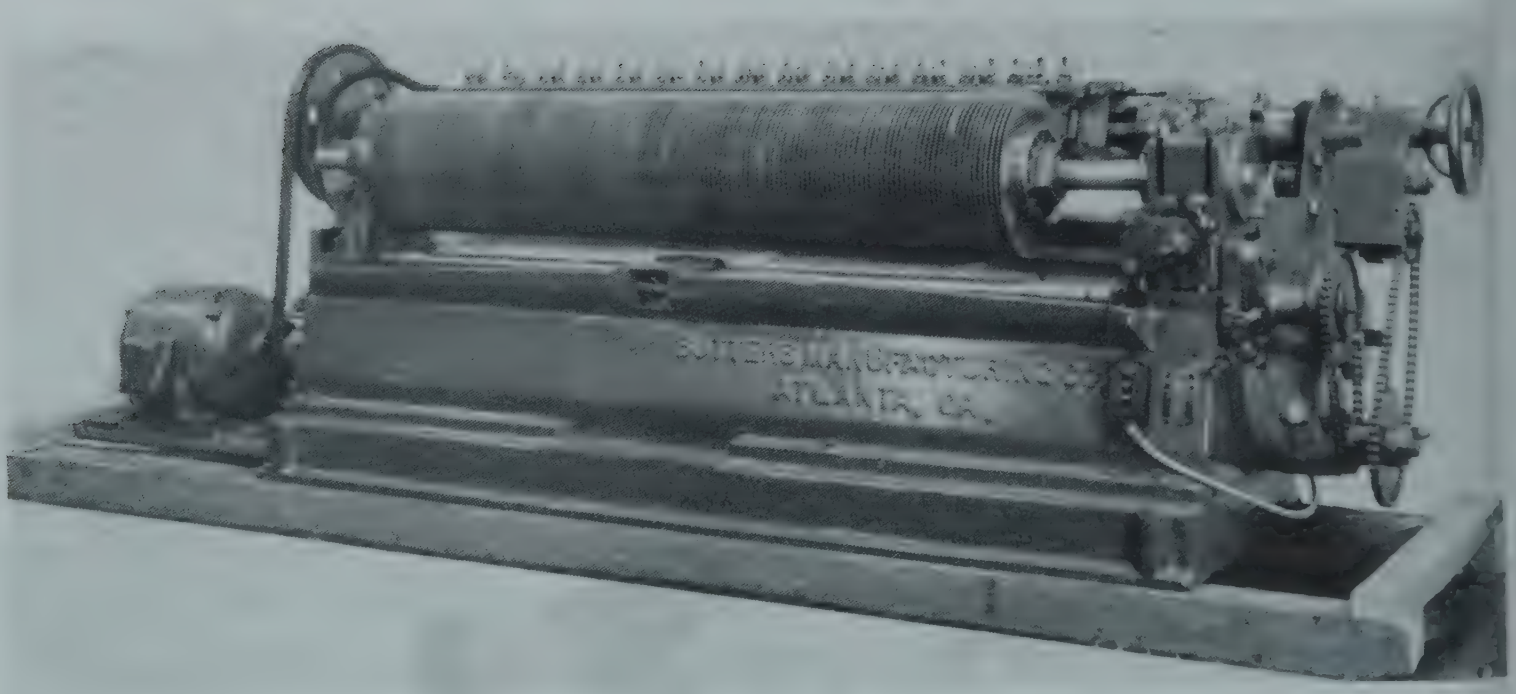


Fig. 138. Milling machine for linter saws.
(Courtesy *Butters Manufacturing Co.*)

The early machines performed both of the operations with a machine having one or several heads which were moved manually from saw to saw. In these machines, the saw cylinder revolved slowly while the side files operated, and the gummer file on a floating spindle engaged the teeth.

The modern filing machine, Figure 136, contains a large number of reciprocating files for the side filing, operating so that six settings will file all the saws on a 141-saw cylinder on both sides.

The modern gumming machine, Figure 137, and the milling machine, Figure 138, are each positively indexed so that the gummer file or milling cutters, as the case may be, accurately engage the teeth in each sharpening operation throughout the life of the saw. The machines usually have 36 spindles, so that the entire cylinder of 141 saws can be sharpened in four revolutions of the cylinder. The entire operation is automatic because the four shifts are performed mechanically. The machines are indexed positively, therefore, they will cut teeth in a blank saw. They will also generate a new tooth in case one is broken off.

C. Lint Cleaning

The extent to which the delinting of cottonseed is practicable was formerly limited. This was due to the fact that, if it was carried too far at high capacity, a great deal of "hull pepper," as well as larger hull

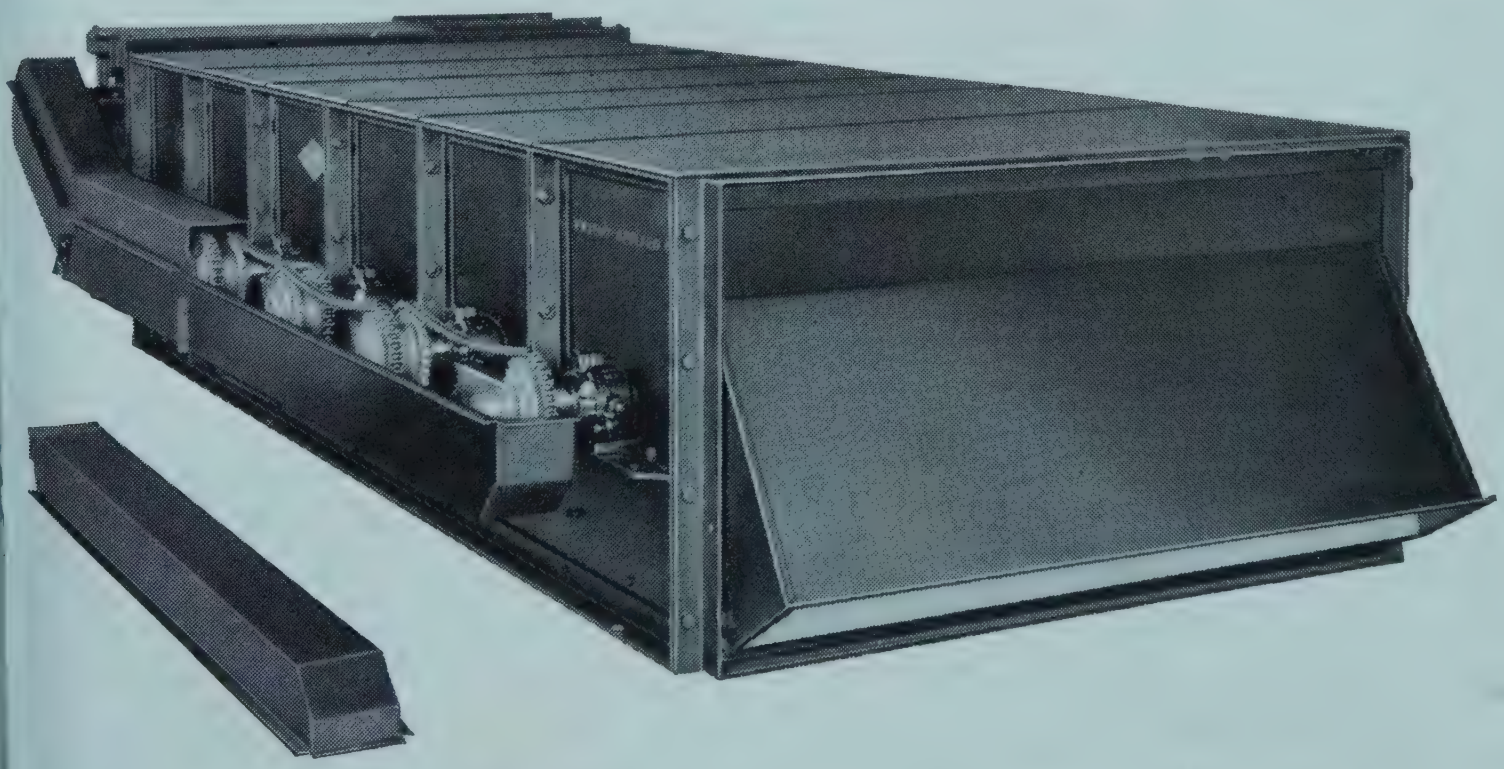


Fig. 139. Lint cleaning machine.
(Courtesy *Carver Cotton Gin Co.*)

particles, were carried over with the lint. Removal of this foreign material was beyond the moting capacity of the linter or the cleaning effect of the condenser, without undue loss of fiber.

Lint can now be collected by a flue collecting system and discharged from a cyclone into lint cleaning machinery, Figure 139, that will remove

these impurities. This has resulted in a positive control of the quality of lint, so that the latter can be sold on the basis of cellulose content for chemical purposes.

Lint cleaning by this machinery is performed by beating the lint over perforated metal screens in combination with pneumatic moting effects.

IV. Hulling and Separation of Cottonseed[7]

A. Hulling

The earliest hullers were of the bar type. One of these machines is illustrated in Figure 140. This machine consisted in part of a frame which held stationary knives running the full width of the huller. These knives

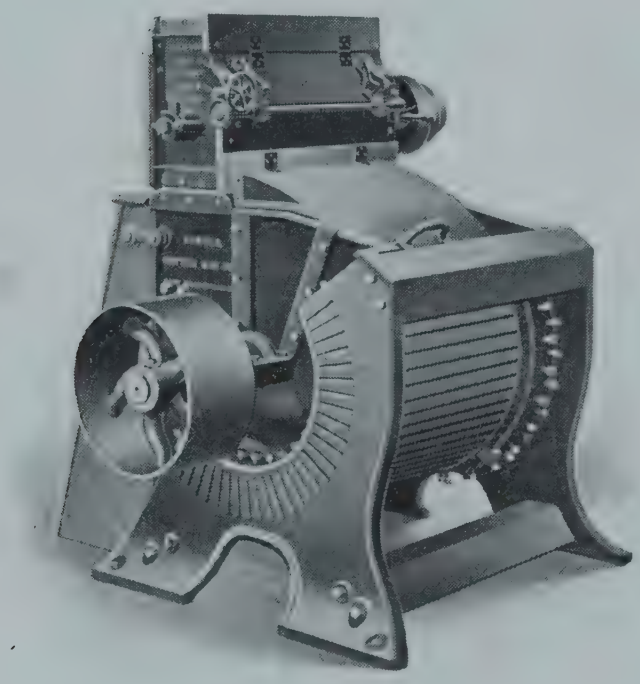


Fig. 140. Early type of bar huller. (Courtesy *Carver Cotton Gin Co.*)

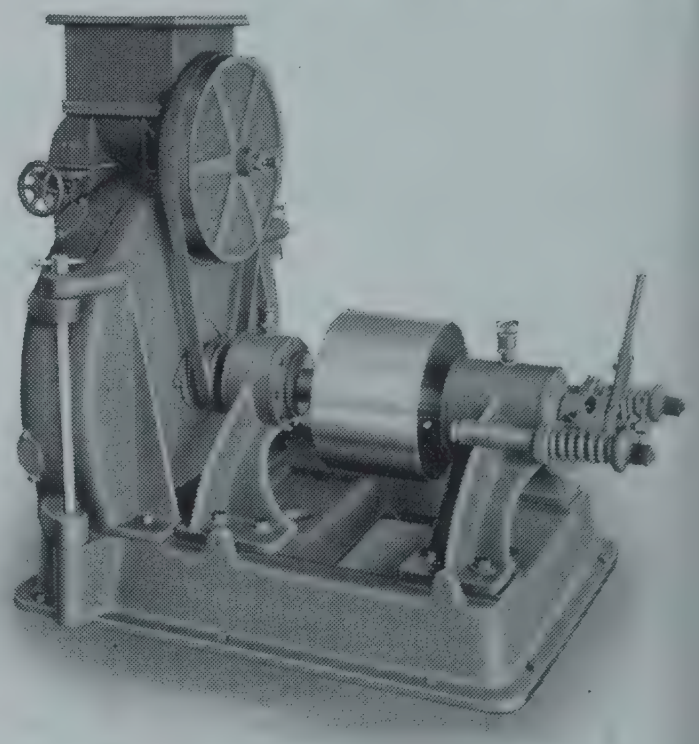


Fig. 141. Disc huller. (Courtesy *Carver Cotton Gin Co.*)

were individually adjustable toward the cylinder. The cylinder was a heavy drum running at high speed with knives the full width of the drum. These knives were usually of I-shaped cross section and were held by plates or clamps.

[7] See also: H. Barned, *Oil Mill Gazetteer,* **39,** 9 (Sept., 1934); E. Bradshaw, *ibid.,* **37,** 6–7 (Aug., 1932), **37,** 5–7 (Nov., 1932), **38,** 8–9 (Dec., 1933), and *Cotton and Cotton Oil News,* **34,** 4 (June 10, 1933); J. P. Dickinson, *Oil Miller,* **16,** No. 2, 19 (1922); H. O. Fulson, *Cotton Oil Press,* **13,** 63–65 (Aug., 1929), **17,** 18 (March, 1934), *Oil Mill Gazetteer,* **34,** 13 (Aug., 1929), and *Oil Miller & Cotton Ginner,* **36,** 20–21 (May, 1930); J. P. Greenwood, *Cotton Oil Press,* **12,** 29–31 (Nov., 1928); P. S. Grogan, *ibid.,* **17,** 26–27 (March, 1934), *Cotton and Cotton Oil News,* **35,** 3–4 (Jan. 23, 1934), *Oil Miller & Cotton Ginner,* **43,** 8–9 (Feb., 1934), and *Oil Mill Gazetteer,* **38,** 11–12 (March, 1934); D. C. Holly, *ibid.,* **38,** 7–8 (April, 1934); L. Johnson, *Cotton and Cotton Oil Press,* **43,** A-7 (Oct. 10, 1942); C. L. Lockett, *ibid.,* **45,** A-9 (June 3, 1944) and *Oil Mill Gazetteer,* **35,** 7 (July, 1930); T. J. McNulty, *ibid.,* **37,** 11–12 (Nov., 1932) and **37,** 17–18 (April, 1933); J. V. Petty, *ibid.,* **40,** 11 (Jan., 1936); O. H. Sale, *ibid.,* **47,** 3 (Sept., 1942); C. N. Volz, *ibid.,* **40,** 17 (June, 1936).

These machines performed well, when in proper adjustment, but required a great deal of attention to maintain adjustment of the stationary knives.

The next popular machine was the disc huller, Figure 141. This machine is similar in operation to an attrition mill, except that the plate on one side is stationary. The disc huller functions, therefore, through the operation of one stationary and one rotating disc, upon the face of each of which

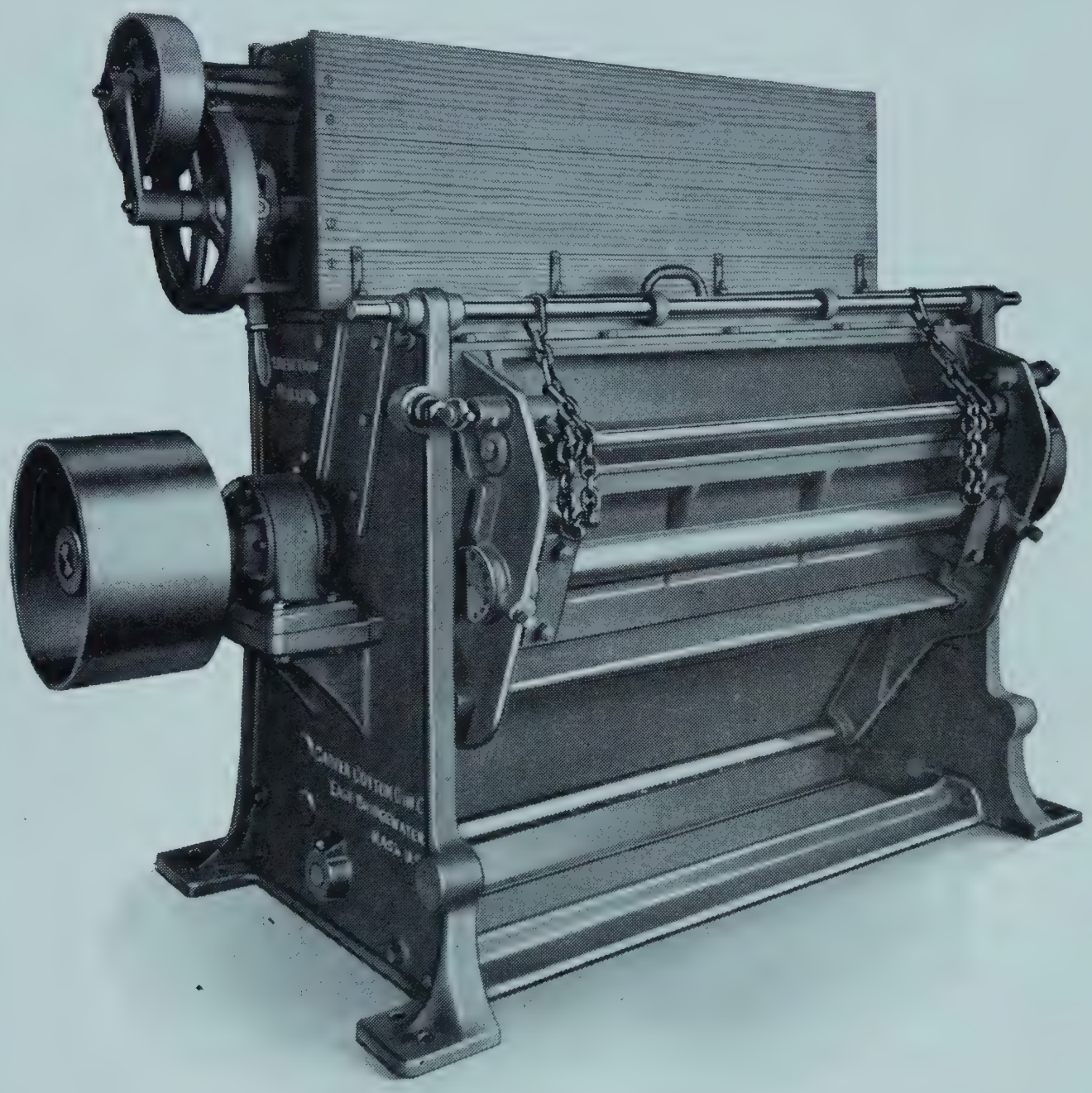


Fig. 142. Modern bar-type huller. (Courtesy *Carver Cotton Gin Co.*)

there are cast bars or ridges with cutting edges radiating from the center. The face of each plate is concave which permits free entry of the seed near the center. The seed then travel centrifugally outward through a gradually narrowing space between discs which are the least distance apart at the periphery where the seed are cleanly cut between the stationary and rotating sharp edges. When speeded in accordance with manufacturers instruction and provided with sharp plates, it delivers the seed in a form excellently adapted for separation.

The bar-type huller came back in favor as a result of improvements in its design. This machine was modernized and much improved by provision for having the entire breast or concave adjustable to the cylinder. This eliminated the tedious individual adjustment of the stationary knives. Inexpensive types of knives which could be reversed and turned over were among the other improvements introduced. Safety features were also provided to take care of accidentally introduced foreign matter.

A modern type of bar huller is shown in Figure 142. This huller will cut the seed with the minimum absorption of oil and can be easily and quickly adjusted.

While the word "cut" has been used in describing both types of hullers, in view of the fact that some cutting must certainly take place, there is evidence to indicate that under optimum operating conditions the hulling process is more a cracking operation than it is one of actual cutting.

Ayres [3] gives the power requirements for a 48-inch bar huller as 15 h.p. Under optimum operating condition, the power requirements will be found to be lower than this figure.

The proper speed for a bar-type huller is about 750 r.p.m. for the 48-inch size handling approximately 75 tons of seed per 24 hours and set to cut or crack approximately 80% of the seed, with return of the uncut seed to the same huller. A 48-inch bar huller will handle considerably more tonnage, however, with very satisfactory results.

B. Separating

The separation of cottonseed meats from hulls should be done in such a manner as to: (*a*) obtain hulls free from whole seed and meats, (*b*) obtain hulls with the lowest possible absorbed oil content, (*c*) obtain meats as free as possible of very fine hull bran fiber and dirt, and (*d*) suitably control the hull content of the meats, in order to regulate the protein content of the finished cake.

The approach to perfection obtainable in the separating process is dependent upon such factors as: (*a*) the moisture content of the seed, (*b*) the amount of linters left on the seed, (*c*) the degree of deterioration of the seed, (*d*) the amount of oil absorbed in the hull of the seed before it reaches the hulling and separating operation, (*e*) the quantity of loose fibers, hull bran, dirt, etc. in the seed, and (*f*) the setup and operating conditions of the separating machinery.

With modern separating equipment of sufficient capacity properly operated on prime seed which contain 10 to 12% moisture and not to exceed 2.5% lint, and are fairly free of broken seed and meats, loose fiber, hull bran, dirt, etc., the total oil left in the hulls should be well under 0.50%. Under less favorable conditions, a value considerably higher than this may be expected.

Although separating processes vary greatly in detail, they fall into the following general classification: (*a*) double hulling, (*b*) single hulling, and (*c*) universal hulling.

1. Double Hulling Process

In this process, the seed is passed through a huller mounted on a shaker separator, Figure 143. The seed are cut coarsely to avoid oil absorption



Fig. 143. Shaker separator for cottonseed.
(Courtesy *Carver Cotton Gin Co.*)

by the hulls, and the free meats are shaken out as the material passes over the shaker separator. The mixture of hulls and uncut seed is passed through a hull beater, Figure 144, to remove fine floury meats. The entire process is then repeated by passing the hulls and uncut seed through a second huller, shaker, and beater. This second huller is set close enough to hull all the remaining seed.

The meats from the shakers are collected and passed over a meats purifier, Figure 145, which consists of several shaking trays equipped with adjustable suction nozzles to scalp off the floating hull particles from the meats layer. The meats from the hull beaters are sometimes purified on a shaker under this machine and then passed to the main purifier with the meats from the shaker separators. In other cases, the meats from the hull beaters are passed directly to the press room.

The hulls lifted from the meats on the purifier are collected in a cyclone and then passed through a small beater having a screen of fine perforated

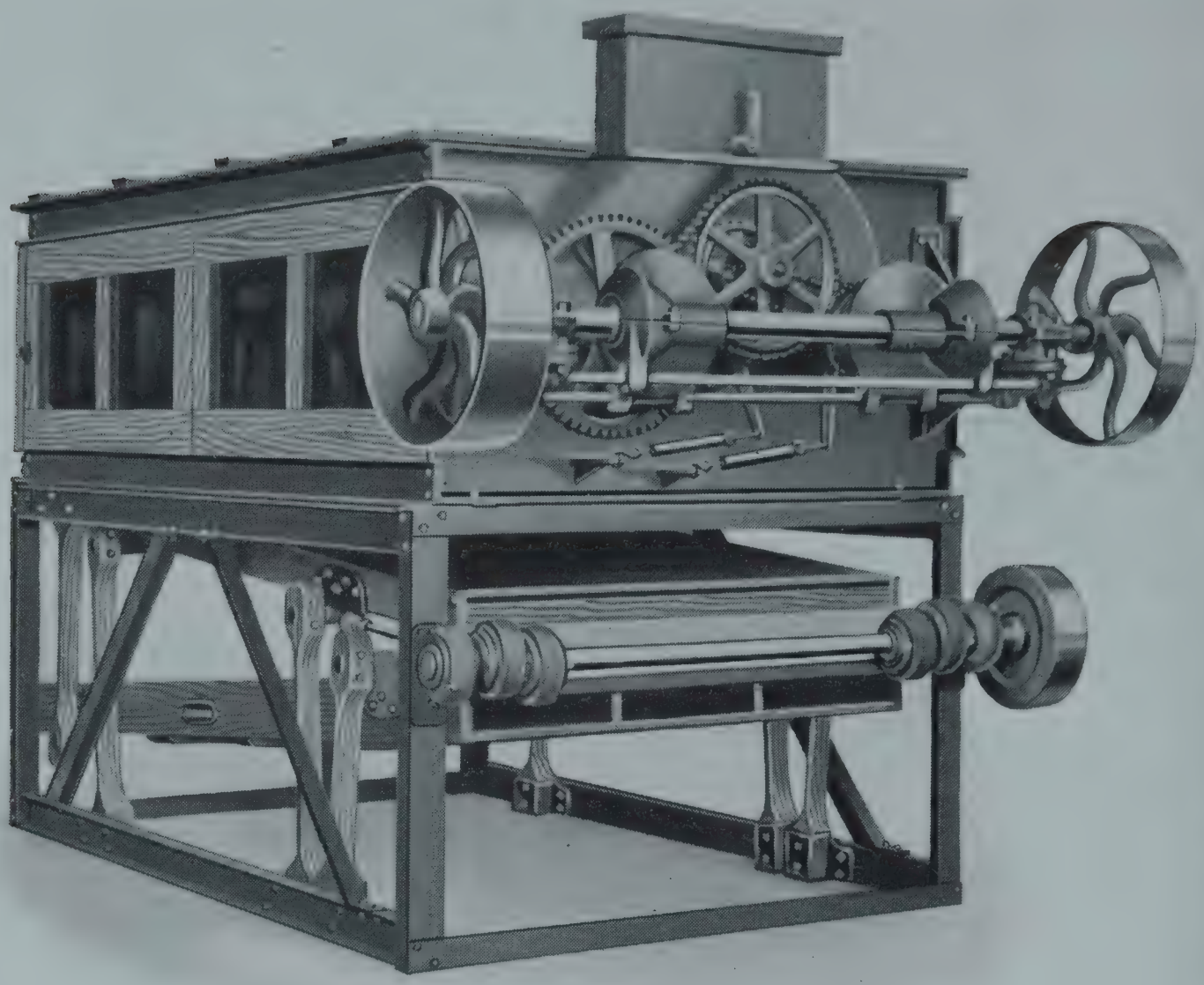


Fig. 144. Hull beater. (Courtesy *Carver Cotton Gin Co.*)

metal to remove fine floury meats. These meats pass to the press room. The hulls from this small beater are collected with the main stream of hulls from the second-cut hull beaters and conveyed to finished hull storage.

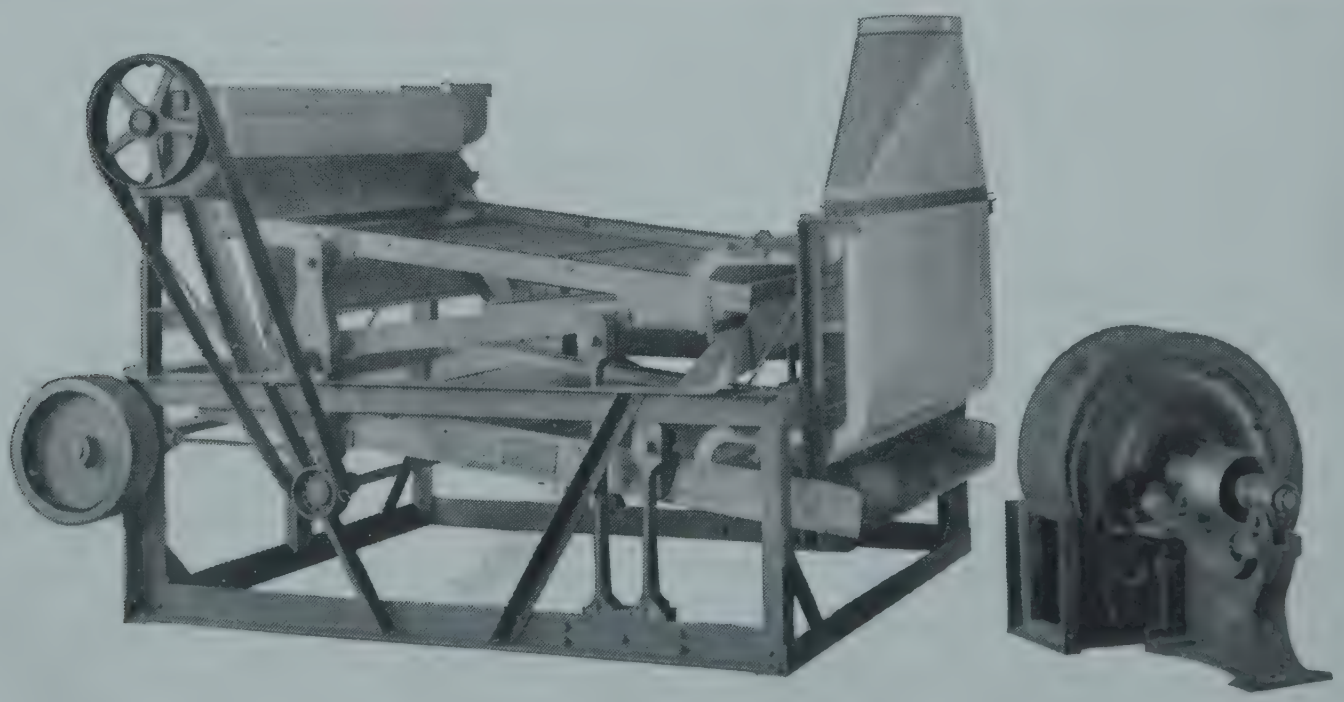


Fig. 145. Cottonseed meats purifier. (Courtesy *Carver Cotton Gin Co.*)

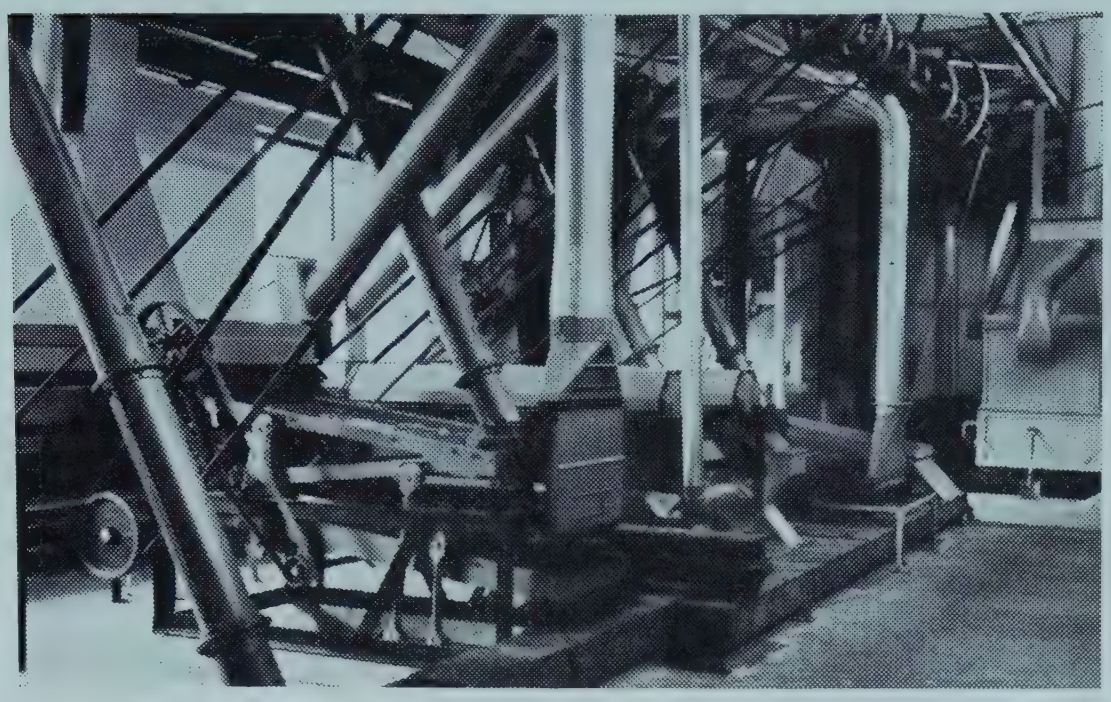


Fig. 146. Single hulling process installation. (Courtesy *Carver Cotton Gin Co.*)

2. Single Hulling Process

It can be seen that in double hulling the entire tonnage of hulls passing over the first-cut shakers and hull beaters is again passed through the second-cut hullers. This second-cut huller has a very close setting; consequently the hulls are exposed to oil absorption a second time in hulling the uncut seed. In order to avoid this, it is desirable to separate the hulls from the uncut seed before going to the second-cut huller and to allow these hulls to go to storage. This is what is accomplished in the so-called single hulling process. An installation using the single hulling process and meats purifier is shown in Figure 146.

In the single hulling process, the seed are passed through a huller, cutting approximately 80 to 85% of the seed in the first pass. The cut seed are then put over a shaker separator to remove the free meats. The hulls and uncut seed are passed through a hull beater and then a hull and seed separator (Fig. 147), to remove the uncut seed. The hulls are conveyed to finished hull storage and the uncut seed are returned to the original huller or hullers.

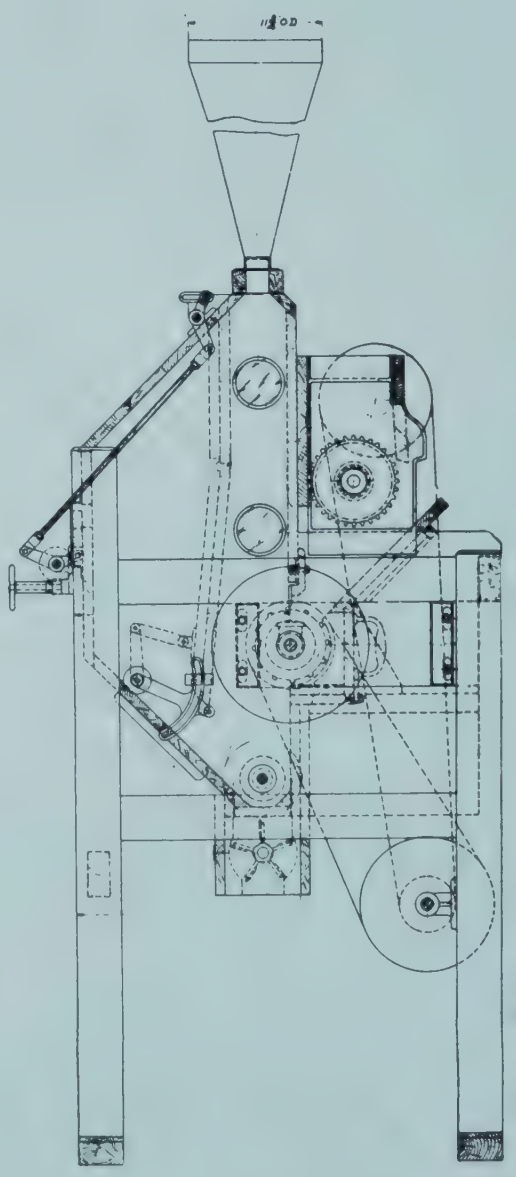


Fig. 147. Hull and seed separator. (Courtesy *Carver Cotton Gin Co.*)

In some cases, a combined shaker and hull and seed separator unit,

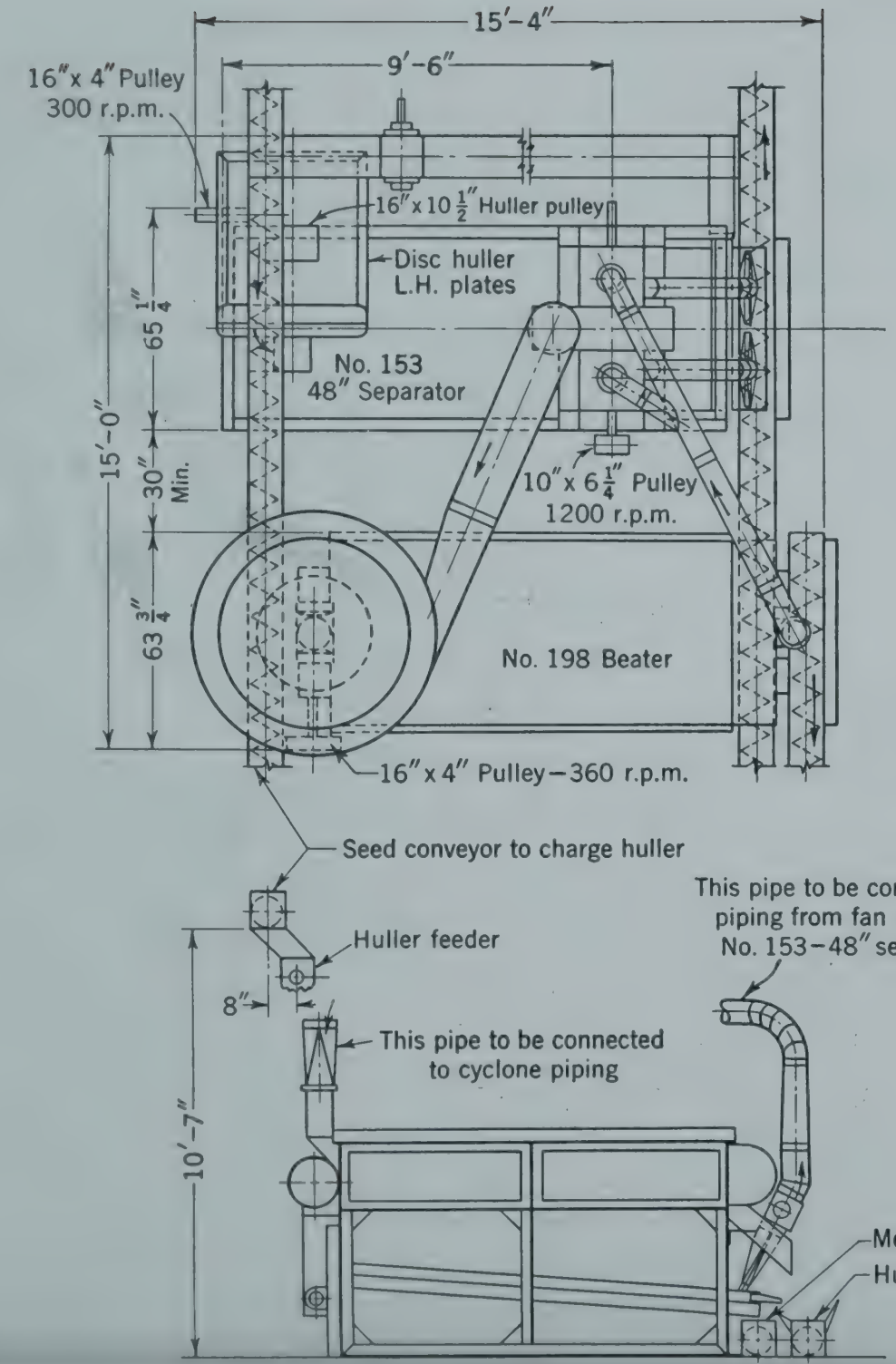


Fig. 148. Combined shaker and hull and seed separator unit. (Courtesy *The Bauer Bros. Co.*)

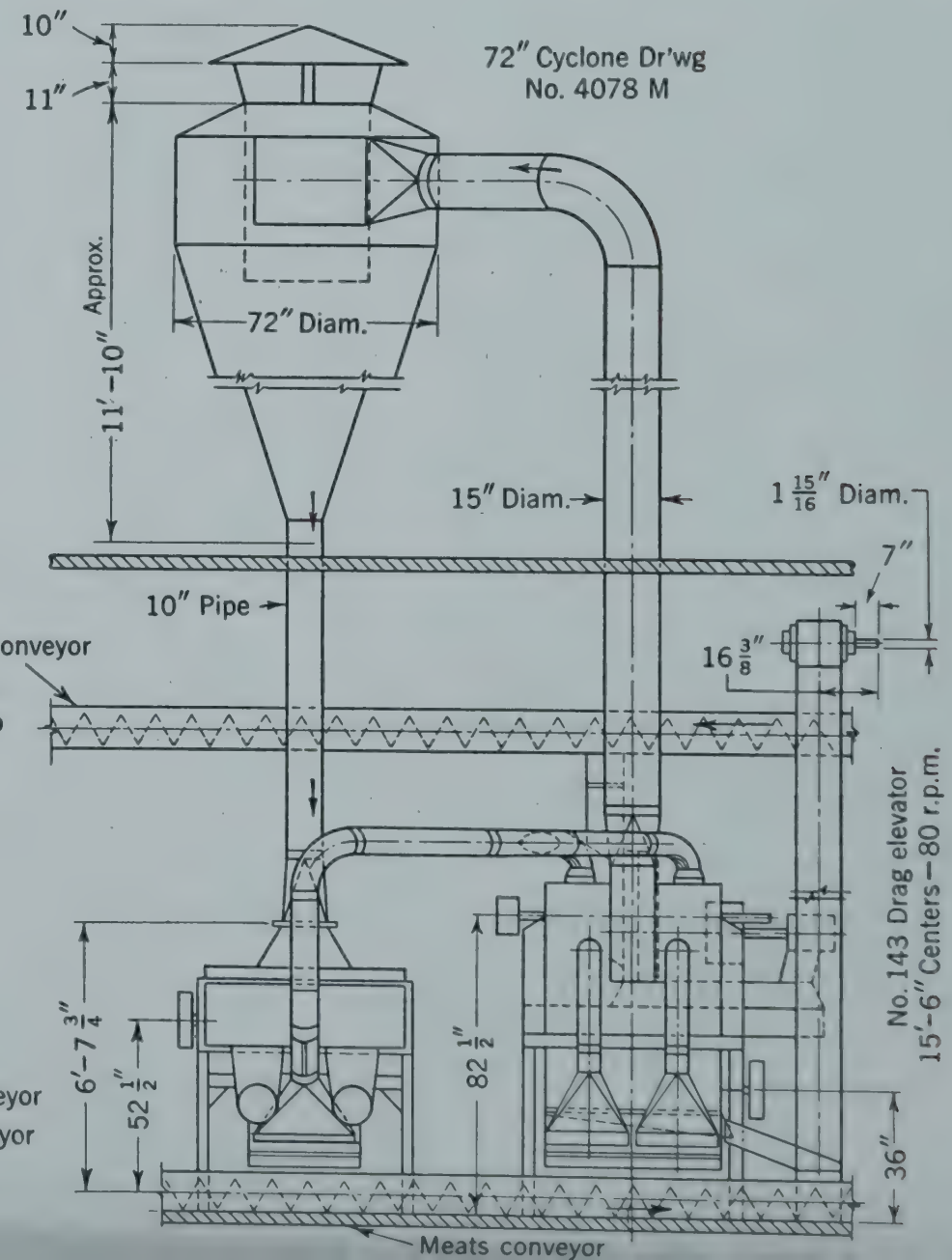


Figure 148, is used, followed by a beater through which the hulls pass before they go to storage.

The shaker separator can be of the purifying type so that the meats are purified on the lower tray by an adjustable air nozzle. In some cases where this is done, the purification is made very drastic so that some meats are picked up with the hulls; the hulls containing some meats are then put over a meats purifier.

When the seed are delinted very closely, the separation of hulls from the meats becomes more difficult than when the hull particles retain considerable lint. This is due to the fact that relatively bare hulls will not mat as easily on the shaker, and also that air nozzles will not lift a smooth hull as easily as a hull with a little residual fiber.

The double hulling process produces a large amount of fine hulls in the second hulling due to the close setting of the huller. These fine hulls are inclined to pass through the perforations of the shaker and are difficult to separate from the meats. On the other hand, with single hulling, all the seed pass through only a coarsely set huller which does not produce these fine hulls. This is a second advantage of the single hulling process which has made this process necessary because of the extremely close delinting carried out in recent years.

3. Universal Hulling Process

The method of universal hulling is a combination of the single and double hulling processes. In this process, the hull fraction from the single hulling operation before going to storage is passed through a second, more closely set huller and a shaker and beater. This modification of the process can be used advantageously in special cases such as the following: (*a*) where a large amount of lint is left on the seed and a relatively low-protein cake is required, and (*b*) where the seed contain a large amount of immature seed.

In the first case, the second huller can be set to deliberately produce fine hulls to dilute the protein content of the cake.

In the second case, the huller can be set very fine to cut the immature seed which may not be separated perfectly in the hull and seed separator.

While this process may appear to be double hulling, the separation of the uncut seed before the second hulling is a distinct advantage from the standpoint of oil absorption loss. As long as normal or high-lint cuts are profitable, there is little need for this process. The presence of a few immature seed in the finished hulls has probably been taken more seriously than is necessary, since these seed contain only a shriveled meat with very little available oil.

4. Power Requirements

The average value for power required to operate separating machines is given by Ayres [3] in the accompanying table.

Machine	Power, h.p.
Hull beater, 2-drum	3
4′ × 12′ shaker	3
Safety shaker	1
Seed separator and fan	4
Purifier and fan	4
Tailings beater	½

5. Operation, General

The difference between machines of different manufacture and the wide variation in the arrangement of the machines and in their operating conditions from mill to mill make it impractical to attempt to describe the size and arrangement of the various screens, the speeds for operating the various parts, and other such details as are required to enable one to set up operating standards for separating machinery in general.

However, the following general remarks may be found useful: (*a*) Any separating arrangement should be as simple as possible; "cure-alls" should be avoided. (*b*) The material should be handled as little and as gently as possible. (*c*) The principal separation is usually accomplished with 7/32-inch round perforated metal, either flat or corrugated depending upon the type of shaker. (*d*) When working seed containing less than 2½% residual lint, more trouble usually results from having too much screening area and metal with openings too small than *vice versa*. (*e*) The direction of rotation of the drum and the spikes of hull beaters should be the same. (*f*) Uniformity of feed is one of the most important factors in the operation of separating equipment.

V. Rolling Cottonseed Meats [8]

A. Nature of the Rolling Process

Prior to about 1930 rolling was thought to be a process whereby the oil-containing cells were actually ruptured.[9] Thornton,[10] and Woolrich and Carpenter,[11] working independently, offered evidence which seemed to

[8] R. G. Reeves and J. O. Beasley, *Cotton and Cotton Oil Press,* **38,** 3 (Dec. 4, 1937). J. L. Rosson, *ibid.,* **37,** 6 (Sept. 6, 1936).

[9] L. L. Lamborn, *Cottonseed Products,* Van Nostrand, New York, 1920.

[10] M. K. Thornton, Jr., *Cottonseed Products,* Oil Mill Gazetteer, Wharton, Texas, 1932.

[11] W. R. Woolrich and E. L. Carpenter, *Mechanical Processing of Cottonseed,* Eng. Expt. Sta., Univ. of Tenn., Knoxville, 1935.

prove that few cells were actually ruptured in the rolling process. However, foreign research workers,[12] between 1925 and 1934 published very convincing proof that a large percentage of the cells were actually ruptured. This leaves the question of cell rupture open; however, experience has shown that cottonseed meats should be rolled to a thickness of between 5 and 10 thousandths of an inch for best results, whether cells are actually ruptured or not. In either event the purpose of rolling seems also to be that of reducing the meats to a physical state which will promote the most efficient contact between the meats and the hot humid vapor under the conditions encountered in the cooking process.

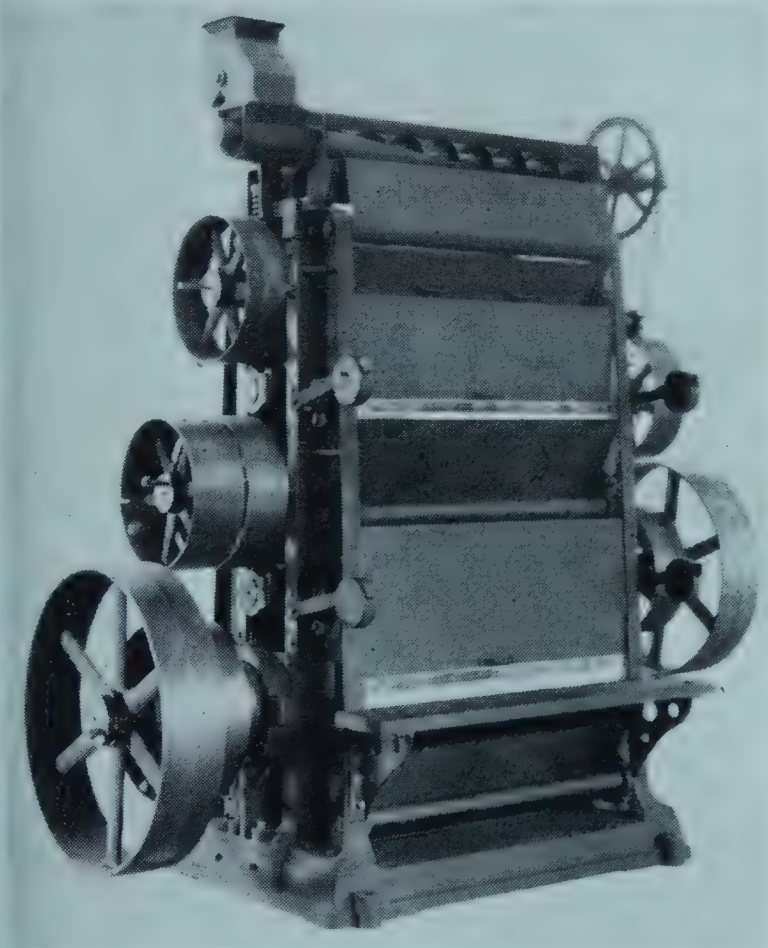


Fig. 149. Cottonseed crushing rolls. (Courtesy *The French Oil Mill Machinery Co.*)

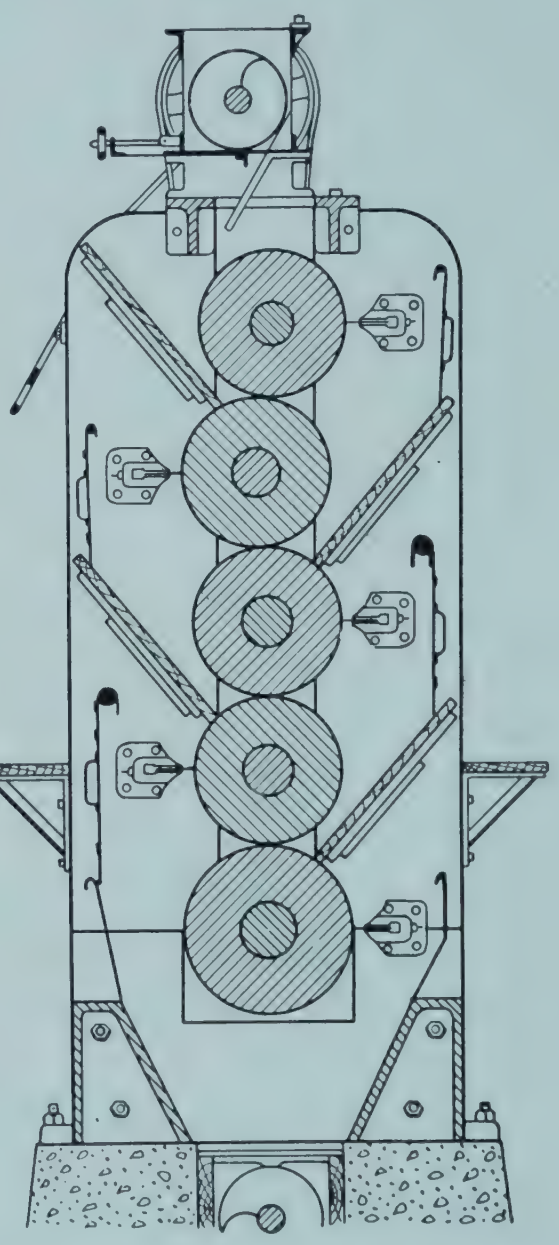


Fig. 150. Cross section of 5-high crushing rolls. (Courtesy *Davidson-Kennedy Co.*)

B. Equipment for Rolling

The type of machine almost invariably used for rolling cottonseed meats in this country is illustrated in Figure 149. A description of the operation of a set of rolls is best understood by referring to Figure 150.

[12] A. M. Goldovskii and M. Podol'skaia, *Masloboino Zhirovoe Delo,* **10,** No. 4, 12 (1934). O. Shchepkina, *ibid.,* **10,** No. 3, 16 (1934). R. Heublyum and H. Japhe, *Allgem. Oel-u. Fett-Ztg.,* **32,** 447–452 (1935).

The meats from the feeder shown on top are distributed uniformly along the top crushing roll. Over this roll they fall to a cant board, which prevents them from falling farther, and directs them to the contact surface between the first and second rolls. The rolling of these two heavy cylinders together, draws in and crushes the meats, passing them through to the other side. Any crushed meats adhering to the back face of the top roll are removed by a stationary scraper and fall, assisted by the cant board—with the meats adhering to the second roll—into the space between rolls two and three. This gives the meats a second crushing; with a stand of five rolls, four crushings are, of course, received by the meats during passage from the top to the bottom. The crushing pressure is due to the weight of the rolls themselves; it increases by the weight of one roll at each successive passage of the meats between a pair of rolls, until at the bottom or last stage the meats are subjected to the combined weight of the four upper rolls.

C. Operation of the Rolls

1. Humidification of Meats

It is the opinion of many successful operators that meats should be rolled to the form of flakes and not to a finely pulverized material, and that in order to produce satisfactory flakes a certain amount of moisture is necessary. If the meats are too dry, sufficient moisture must be added before rolling to produce proper flaking. The addition of moisture to meats is not an easy thing to accomplish in a completely satisfactory manner; however, it is not impossible, and considerable benefit will result if it is properly done. A detailed description of one successful means of adding moisture to meats before rolling is given in an article by Wamble.[13]

2. Flake Thickness vs. Extraction Efficiency

The effect of flake thickness upon extraction efficiency and oil quality is illustrated by typical data shown in Table 164. The two tests of this table were run several months apart in the same plant; test *1* being on seed from one crop, and *2* on seed from another crop. The plant was so arranged that the meats from the separating department could be divided equally between two sets of rolls and, from that point, processed in identical equipment. In other words, all factors except the thickness of the flakes were as nearly alike in each of the two tests as one might expect to have them in a commercial plant under actual operating conditions.

[13] A. C. Wamble, *Oil Mill Gazetteer*, **49**, 24–28 (Sept., 1944) and *Cotton and Cotton Oil Press*, **45**, A-3, A-4, A-6 (Sept. 23, 1944). See also F. L. Woodward, *Oil Mill Gazetteer*, **37**, 19–20 (April, 1933).

TABLE 164

Effect of Flake Thickness upon Extraction Efficiency and Oil Quality in the Hydraulic Processing of Cottonseed

Measurement	Flake thickness, inch			
	0.013–0.020	0.010–0.013	0.013–0.020	0.010–0.013
	Test *1*		Test *2*	
Analysis of cake				
Moisture, %	5.76	6.14	6.32	6.52
Oil, %	5.96	5.56	6.32	5.80
Ammonia, %	8.31	8.22	8.16	8.18
Press room standard	72	68	78	65
Analysis of oil				
FFA, %	1.0	1.1	2.2	2.2
Refining loss, %	6.2	6.5	10.3	10.0
Color Lovibond red	5.0	5.0	6.6	6.8

3. Capacity and Roll Efficiency

For efficient rolling, a good feeder over the top roll is necessary. The rolls themselves must be kept in exact alignment, truly ground, and free from pits or cracks; the scrapers must remove all meats that adhere to the roll surface; no leaks by either the ends of the rolls or the cant board can be tolerated. The stream of meats passing through should never be allowed to become too thick at any point, since matting of the meats will destroy most of the flaking effect.

The size, speed, and general design of rolls greatly affect their capacity. Under the most favorable conditions possible, a set of rolls might be expected to handle 1 pound of meats for every 50 square feet of roll surface

TABLE 165

Efficiency Obtained in the Rolling of Cottonseed Meats

Mill no.	Bottom roll			Pounds of meats per min.	Thickness of flakes, 1/1000 in.		Efficiency, %
	Length, in.	Diameter, in.	Speed, r.p.m.		Theory	Actual	
1	60	18	178	110	6	9–12	57
2	60	20	205	140	6–7	8–12	65
3	60	18	198	70	3–4	9–11	35
4	60	20	273	140	4–5	7–9	56
5	60	18	209	110	5–6	4–21	44
6	60	18	270	110	4–5	7–8	60
7	60	18	270	140	5–6	9–15	46
8	60	20	140	90	6	10–13	51
9	60	20	165	100	5–6	9–14	48
Average							51

generated by the bottom roll, and produce flakes as thin as 0.005 inch (assuming that the flakes have a density of 48 pounds per cubic foot). In theory, a thickness of 0.005 inch is possible under the conditions outlined; however, in practice, it has been found that the rolling operation

TABLE 166

Table for Determining the Size and Speed of Rolls for Producing Cottonseed Flakes of Specified Thickness under Different Conditions

Diameter and weight per inch	Expected thickness of flakes, 1/1000 in.	Length of rolls, inches						
		24	30	36	42	48	54	60
		Revolutions per pound of feed[a]						
14 inches 50.8 pounds	2	32.7	26.2	21.8	18.7	16.4	14.6	13.1
	4	16.4	13.1	10.9	9.4	8.2	7.3	6.6
	6	10.9	8.7	7.3	6.2	5.5	4.9	4.4
	8	8.18	6.54	5.46	4.68	4.10	3.64	3.28
	10	6.55	5.24	4.37	3.74	3.27	2.91	2.62
	12	5.46	4.37	3.64	3.12	2.73	2.43	2.18
	14	4.68	3.74	3.12	2.67	2.34	2.08	1.87
	16	4.09	3.27	2.73	2.34	2.05	1.82	1.64
	18	3.64	2.91	2.43	2.08	1.82	1.62	1.36
	20	3.27	2.62	2.18	1.87	1.64	1.46	1.31
16 inches 66.7 pounds	2	28.6	22.9	19.1	16.4	14.3	12.7	11.5
	4	14.3	11.4	9.6	8.2	7.2	6.4	5.7
	6	9.5	7.6	6.4	5.5	4.8	4.2	3.8
	8	7.16	5.72	4.78	4.10	3.58	3.18	2.86
	10	5.73	4.58	3.82	3.27	2.86	2.55	2.29
	12	4.77	3.82	3.18	2.73	2.39	2.12	1.91
	14	4.09	3.27	2.73	2.34	2.05	1.82	1.64
	16	3.58	2.86	2.39	2.05	1.79	1.59	1.43
	18	3.18	2.55	2.12	1.82	1.59	1.42	1.27
	20	2.86	2.29	1.91	1.64	1.43	1.27	1.15
18 inches 83.3 pounds	2	25.5	20.4	16.8	14.6	12.7	11.3	10.2
	4	12.7	10.2	8.5	7.3	6.4	5.6	5.1
	6	8.5	6.8	5.7	4.7	4.2	3.8	3.4
	8	6.36	5.10	4.24	3.64	3.18	2.82	2.54
	10	5.09	4.07	3.40	2.91	2.55	2.26	2.04
	12	4.24	3.40	2.83	2.43	2.12	1.89	1.70
	14	3.64	2.91	2.42	2.08	1.82	1.62	1.45
	16	3.18	2.55	2.12	1.82	1.59	1.41	1.27
	18	2.83	2.26	1.89	1.62	1.42	1.26	1.13
	20	2.55	2.04	1.68	1.46	1.27	1.13	1 02
20 inches 108.3 pounds	2	22.9	18.4	15.3	13.1	11.5	10.2	9.2
	4	11.4	9.2	7.6	6.6	5.7	5.1	4.6
	6	6.6	6.1	5.1	4.4	3.8	3.4	3.1
	8	5.72	4.60	3.82	3.28	2.86	2.54	2.30
	10	4.58	3.66	3.06	2.62	2.29	2.04	1.83
	12	3 82	3.06	2.55	2.18	1.91	1.70	1.53
	14	3.27	2.62	2.18	1.87	1.64	1.45	1.31
	16	2.86	2.30	1.91	1.64	1.43	1.27	1.15
	18	2.55	2.04	1.70	1.46	1.27	1.13	1.02
	20	2.29	1.84	1.53	1.31	1.15	1.02	92

[a] Based on an assumed flake density of 50 lb. per cu. ft. and 50% rolling efficiency

is on an average only about 50% efficient (see Table 165). This means that one must either figure on twice as much roll surface being generated as would be indicated by the above theoretical thickness calculations,[9] or that the actual thickness of the flakes can be expected to be in the neighborhood of twice what the theoretical calculation would indicate.

On the basis of the results shown in Table 165 and similar data on rolls of lengths other than 60 inches, it may be assumed that the use of an efficiency factor of 50% for the purpose of rating rolls on this type of work is justified.

Table 166 has been worked out on the basis of the above figures and is quite useful for the purpose of determining the size and speed of rolls required to produce a certain thickness of flakes under a given set of conditions. The use of the table is quite simple, for example, a mill has rolls 20 inches in diameter by 60 inches long which are fed at the rate of 100 pounds of meats per minute—this mill wishes to roll to a thickness of 0.008 inch; it is desired to know at what speed the bottom roll should be run. The answer may be found as follows: consulting Table 166 under "diameter" (extreme left column) find 20; under "thickness" (2nd column from left) find 8; then follow across on line with 8 to the extreme right column and under "length" of 60 find the figure 2.30 (revolutions per pound of feed); multiply this figure by the pounds of meats per minute ($2.30 \times 100 = 230$) to obtain the recommended speed of 230 r.p.m.

Roll ratings as determined by use of Table 166 will not necessarily check with the ratings given in manufacturers' catalogues or in previously published works on the subject. Thornton,[10] and Woolrich and Carpenter [11] state the capacity of rolls as not to exceed the equivalent of 1½ tons of

TABLE 167

Manufacturers' Ratings of Cottonseed Crushing Rolls in Comparison with Expected Flake Thickness at Rated Capacities as Calculated from Table 166

Measurement	Size of roll, inches					
	Standard design				Heavy type	Extra-heavy type
	36	42	48	60	60	60
Number and length of upper rolls	4-14″	4-14″	4-14″	4-14″	4-16″	1-16″
Number and length of lower rolls	1-16″	1-16″	1-16″	1-16″	1-18″	4-20″
Speed of bottom rolls, r.p.m.	180	180	180	180	180	170
Capacity tons seed per 24 hrs.	40	60	80	100	110	160
Expected thickness of flakes from Table 166 (in 1/1000 in.)	8–9	10–11	12–13	12–13	12–13	16–17

meats per inch of length per 24 hours; such a statement is of very little value.

Discrepancies in manufacturers' ratings are revealed by Table 167 which includes manufacturers' ratings data, and for comparison, expected flake thickness calculated in each case by use of Table 166.

While the data presented represent only a limited number of cases, it has all been obtained in commercial plants under actual operating conditions and is believed to be the most reliable information available on the subject to date.

4. Power Requirements

The power required to operate rolls depends upon the design and mechanical condition of the rolls, as well as the speed and amount of material being processed, the condition of the material, and the uniformity of the feed. The power required to operate a set of 42-inch five-high rolls has been given as 40 h.p. by Ayres,[3] with no other details being stated. Considerable variation has been noted in the power requirements of 60-inch five-high rolls with 18-inch bottom rolls and 16-inch upper rolls operating at speeds of 180 to 200 r.p.m. (bottom rolls) and handling the meats from 90 to 100 tons of Mississippi Delta cottonseed per 24 hours. The power requirements for rolls falling within the above classification have been found to be from 35 to 65 h.p.

D. Importance of Good Roll Operation

The inexperienced and the uninformed are inclined to consider the rolling process as one of the simplest operations in the entire process of converting cottonseed, and one which requires a minimum of thought and attention on the part of the operator. Nothing could be further from the truth. Rolling, if properly done, is a most delicate operation and is very responsive to regular, careful, and intelligent attention. Many of the causes of the great differences in results between well-operated and poorly operated plants are traceable to the rolling operation.

CHAPTER XV

COOKING OF MEATS AND RECOVERY OF THE OIL

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I. Historical

It is reported that as early as 1769 a sample of cottonseed oil was presented to the American Philosophical Society by Dr. Otto of Bethlehem, Pennsylvania. Several years later, in 1783, the Society of Arts, in London, concluded that the oil contained in cottonseed was of commercial value and offered a gold medal as a prize for the production of a ton of cottonseed oil.

The hydraulic press, most commonly used for expression of the oil from cooked meats, was invented in England by Dr. Joseph Bramah in

TABLE 168

Amount of Cottonseed Crushed and Number of Active Mills, 1830–1945[a]

Year	Cottonseed produced, 1000 tons	Cottonseed crushed, 1000 tons	Active cottonseed mills
1830	366[b]	—	[c]
1860	1921	—	7[d]
1870	2012	80[e]	26[d]
1880	3039	182	45[d]
1890	4093	1023	119
1900	4830	2415	357
1910	5175	4106	—
1917	—	—	763
1920	5074	4013	—
1930	6590	5016	520
1940	5259	4151	446
1944	—	—	—
1945	4901[f]	4253[g]	382

[a] *Cotton Production and Distribution*, U.S. Bureau of the Census.
[b] Calculated amount.
[c] Industry in an experimental stage.
[d] L. L. Lamborn, *Cottonseed Products*, Van Nostrand, New York, 1904.
[e] D. A. Tompkins, *Cotton and Cotton Oil*, D. A. Tompkins, Charlotte, N.C., 1901.
[f] *The Fats and Oil Situation*, Bureau of Agricultural Economics.
[g] *Facts for Industry*, U.S. Bureau of the Census.

1795. The first screw press was patented by Whiting in 1799, although it is reported to have been unsuccessful.

The first commercial oil mill in the United States was built about 1801. The oil is reported to have been used for paints and in lamps. By 1830, the United States' production of cottonseed is reported to have been 366,000 tons and exporters were shipping bald seed from Sea Island cotton to Europe.

From these early beginnings, the processing of cottonseed for the recovery of oil has grown steadily as indicated in Table 168.

The striking feature of the history of oil recovery from cottonseed is that, in over a hundred years of commercial experience in the United States, all the seed have been processed by mechanical methods which leave a considerable quantity of oil in the expressed cake. To date, 1945–46, there has been no successful commercial solvent extraction unit in operation on cottonseed, although several continuous units are reported now under construction and may be in operation during the 1946–47 crop season.

II. Hydraulic Processing

A. Rolling of Meats

In the previous chapter on mechanical pretreatment of cottonseed, the importance of proper rolling of the purified meats was discussed. This step prior to the cooking of cottonseed meats is so important to good oil recovery by hydraulic methods that it deserves re-emphasis.

Some investigators claim that the purpose of rolling cottonseed meats to an average flake thickness of about 0.008 inch is to give a large surface area to the meats, so that the cooking process can effectively rupture the oil cells.[1, 2] Other Russian [3] and United States [4] investigators insist that rolling ruptures most of the oil cells and that relatively few are ruptured during the cooking and pressing operators. Mill operators know that the difference between excellent press room work and passable or poor work may be due to: (*a*) a single worn roll, (*b*) too many uncut seed in the feed to the roll, (*c*) unrolled meats escaping through the chipped ends of a roll. (*d*) poor rolling due to too many hulls in the meats, or (*e*) poor distribution of the feed to a roll.

The important point is that rolling must produce uniform thin flakes; otherwise cooking and subsequent pressing cannot be effective.

[1] W. R. Woolrich and E. L. Carpenter, *Chem. & Met. Eng.*, **40,** 291–292 (1933).
[2] M. K. Thornton, Sr., *Oil Miller & Cotton Ginner,* **36,** No. 4, 15–17 (1930).
[3] A. M. Goldovskii, *Masloboino Zirovoe Delo,* **12,** 227–232 (1936).
[4] R. G. Reeves and J. O. Beasley, *Cotton and Cotton Oil Press,* **38,** No. 49. 3 (1937).

B. Prehumidification of Meats

A variety of methods have been used to humidify low-moisture cottonseed or cottonseed meats to a moisture level of about 11% before the meats go to the rolls. A method and apparatus for humidifying meats is described by Graebe,[5] who claims a materially increased oil yield. Briefly, the process consists of spraying water or wet steam into a conveyor containing the hulled meats, and then allowing the wetted mass to stand in a bin one or more hours to disperse the moisture uniformly throughout. This method is said to have the objection that the meat fines, which result from hulling very dry seed, absorb a disproportionate amount of the water and cause an appreciable increase in the free fatty acid content of the oil in this fraction of the meats. A similar result is obtained when rolled meats are humidified and allowed to stand, or when an overflow pile of rolled meats is allowed to "stand" several hours.

A better practice, which aids in hulling (producing a lower separation loss), rolling, and cooking, is to humidify delinted cottonseed by means of wet steam, and then allow sufficient time for the moisture to penetrate the hull coat and so humidify the meats. This practice prevents shattering of dry meats in the huller (which causes high oil loss in the hulls), facilitates effective removal of hulls from meats, and helps to produce thin rolled flakes of suitable moisture content (about 11% is desirable) for further treatment in the cookers. A suitable "delinted seed conditioner" is described by Woolrich.[6] It consists of an enlarged section in a conveyor. The same principle applied to "rotolifts" has been found to be even more effective.

C. Cooking Cottonseed Meats for Hydraulic Pressing

A relatively short number of years ago the proper cooking of cottonseed meats was considered an art, and in some oil mills today it is still so considered. Usually the meal cook had acquired by experience the "feel" and "smell" of properly cooked meats, and the press room results were largely dependent on his acquired skill. The meal cook was in charge of the press room crew, and he told the men when to change the presses after each "layout" time between batches.

The control of cooking by "feel" has been eliminated in many of the mills during the past 15 years. Considerable experimental work has been done by the chemical engineering staffs at several southern universities and also by private organizations. The results of much of this work have been published, so that today there is available a background of better understanding of the reasons for cooking cottonseed meats by certain definitely controlled methods.

[5] H. C. Graebe (to Procter & Gamble Co.), U.S. Pat. 1,707,949 (1929).
[6] W. R. Woolrich, *Mech. Eng.*, **61,** 131–135 (1939).

1. Reason for Cooking Cottonseed Meats

The reason for cooking cottonseed meats have been discussed by several investigators.[1, 4, 7] The consensus of these men is, briefly, that the objects of cooking are:

(*a*) To rupture or finish the rupturing of oil cells.

(*b*) To increase the fluidity of the oil by increase in temperature.

(*c*) To coagulate or granulate the protein aleurone grains. This facilitates a separation of the oil from the proteinaceous and other materials.

(*d*) To "precipitate" phosphatidic material in order to produce oil of lower refining loss.

(*e*) To dry the cooked meats mass to a proper moisture content, optimum for cake compression in the hydraulic press and for oil expression. This prevents "crawling" of wet meats (which is destructive to press cloths), or "crumbling" of dry meats.

(*f*) To detoxify free gossypol by causing this material to diffuse from the resin glands and combine with proteinaceous material to form inert nontoxic "bound" gossypol.

(*g*) To destroy molds and bacteria.

Cooking causes darkening of the oil and cake [4, 8] through diffusion of coloring materials from the resin glands, and also denatures the proteins.

2. Equipment for Cooking

The equipment used for cooking cottonseed meats, in oil mills in the United States, preparatory to hydraulic pressing is usually one of the following types: (*a*) single "batch cooking" kettles, which deliver to a central charging kettle; (*b*) three- to six-high stack cookers, which may be operated as either batch cookers or continuous cookers; and (*c*) pressure cookers.

Relatively few single batch cookers are now in operation. Usually two or more of these steam-jacketed kettles were arranged so that each could be discharged to a centrally located charging kettle. The cooked meats were dropped from the charging kettle to the cake formers and then to the presses.

3. Stack Cooking

(a) Design and Operation of Stack Cooker. The cooker generally used today is the 4- or 5-high stack cooker, a phantom view of which is shown in Figure 151. The individual kettles are usually from 72 to 84 inches in inside diameter and about 28 inches high. The kettles are steam-jacketed on both sides and bottom, as shown in the figure. Each kettle contains an

[7] M. K. Thornton, Jr., *Oil & Soap,* **14,** 151–152 (1937).
[8] M. K. Thornton, Jr., *Oil & Soap,* **11,** 209, 216 (1934).

agitator arm, to which a variety of plows may be attached; these provide constant and thorough mixing of the meats, for efficient heat transfer from the steam-jacketed walls and bottoms to the meats mass.

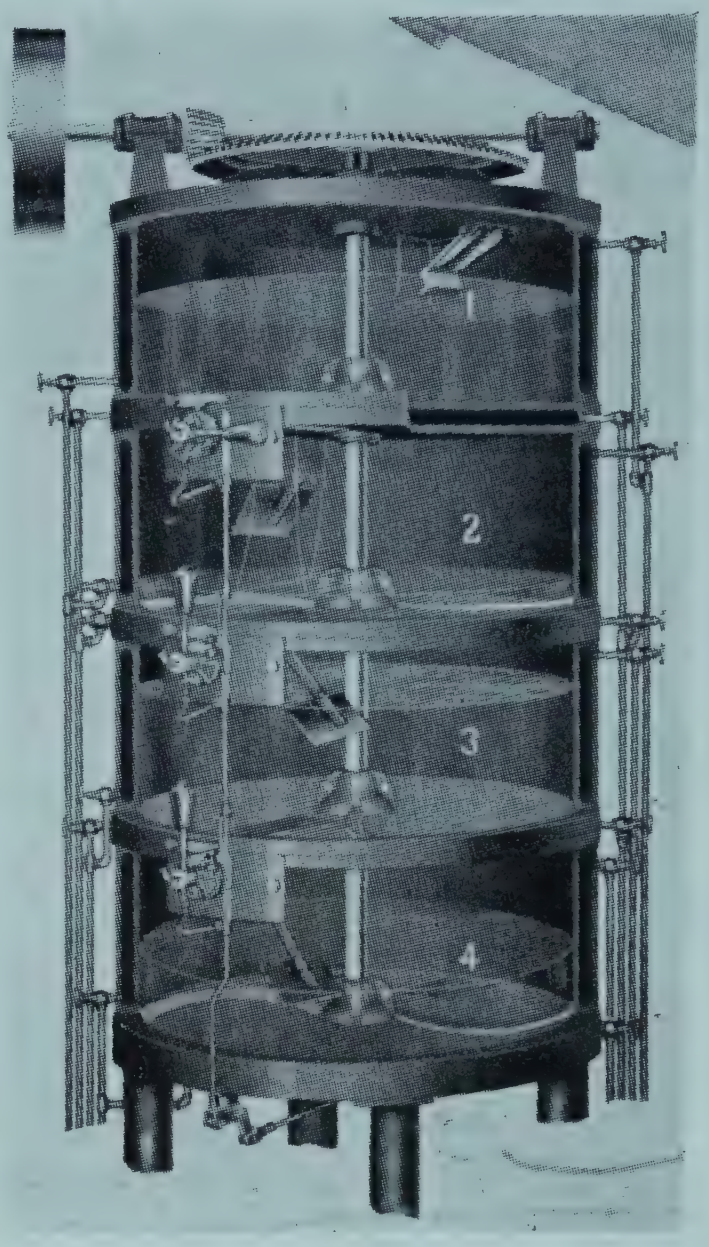


Fig. 151. Phantom view of cottonseed stack cooker with quick-closing gates. Top kettle (1) filling; kettle (2) empty, gate open; kettle (3) full, gate closed; bottom kettle (4) being emptied, gate closed. (Courtesy *The French Oil Mill Machinery Co.*)

Cottonseed meats are not a good conductor of heat, as has been shown by Woolrich and Carpenter[9] and others, hence thorough agitation of the meats is necessary to obtain uniform cooking. A five-high, 84-inch cooker requires a 60-h.p. motor for operation of the agitator arms and plows. Normally, an agitator speed of 35 r.p.m. gives the desired temperature of meats in the kettles with a gage steam pressure of 80 to 100 pounds. By adjustment of the steam pressure, agitator speed (with proper plows), and height of meats in the kettle, it is possible to obtain a fairly wide range in the meats temperature in the kettles.

A five-high stack cooker may be operated as a continuous cooker or, when equipped with quick-closing gates, as a batch cooker. When operated as a continuous cooker, the gate floats are set to maintain a certain meats level in each kettle (the height may be different in each kettle). As a portion of cooked meats is withdrawn from the bottom kettle, an equal quantity cataracts from each kettle to the one below it. This method of processing is often used where the press charging schedule has been set at a definite *continuous* rate. It is desirable to maintain a fairly high meats load in each kettle with continuous cooking, since it has been shown by the use of colored meats or other materials that these may pass through the cooker in periods ranging as widely as 15 minutes to several hours from the time they are added to the top kettle. These tests suggest that a mixture of relatively uncooked and overcooked meats may result from continuous cooking. Aside from the matter of pressing efficiency, the presence of

[9] W. R. Woolrich and E. L. Carpenter, *Mechanical Processing of Cottonseed*, Eng. Expt. Sta., Univ. Tenn., Knoxville, 1935, p. 81.

uncooked meats is important in that it may produce a press cake which is high in *free* gossypol content. With proper control, however, continuous cooking produces good press room results and entirely satisfactory products.

The stack cooker may be operated as a batch cooker when it is equipped with quick-closing gates. When so operated, a definite meats level is maintained in each kettle. When the bottom kettle has been emptied, the operator pulls a lever successively releasing the gates of the kettles above; this allows the meats from each kettle to fill the one below, after which the gates again close. The meats are thus cooked a definite length of time in each kettle and cannot cataract continuously through the cooker. Experience in mills indicates that very satisfactory press room results are obtained with this type of cooking.

Another type of stack cooker [10] has been designed to pass superheated or saturated steam at a temperature in excess of 400° F. directly through the meats in the top two kettles of the cooker, from the bottom upwards. The steam enters the kettles through the agitator shaft and perforated agitator arms. The excess steam and moisture is removed by a ventilating fan. The following advantages are claimed: (*a*) a shorter cooking time, with lower power usage; (*b*) better moisture control of the cooked meats; and (*c*) production of oil of lower refining loss.

(b) Moisture Control during Cooking. It is desirable to have flaked cottonseed meats of 11 to 12% moisture content in the top kettle of a 5-high stack cooker. To obtain uniformity of processing, it is desirable to feed the mill from a seed bin, so that the moisture content and quality of the seed will be fairly uniform. Frequent analysis of the flaked meats for moisture content will indicate the amount of humidification necessary.

Various methods of humidification before rolling have been developed, as mentioned above. When the flaked meats are further humidified, this is generally done by means of a series of calibrated atomizing sprays located in a conveyor just before the top kettle of the cooker. In some mills the flaked meats are humidified by hot or cold water, from calibrated spray nozzles operated by steam pressure, in the top kettle of the cooker.

Uniform moisture control during cooking is essential for good press room work. Accordingly, both humidified meats and cooked meats are sampled at regular intervals for analysis. The time required for analysis is usually two or more hours, so that the results are of value only as a general guide.

To eliminate the uncertainty resulting from delay in analysis and to show constantly the moisture conditions in the various kettles, indicating and recording instruments have been developed which show directly the per

[10] J. Davidson (to Davidson-Kennedy Co.), U.S. Pat. 1,724,073 (1929).

cent moisture in the meats. A number of electrodes are installed in the various kettles, and by means of these the conductance of an electric current through the meats is measured. Some installations have been further equipped with motor-operated valves to maintain the moisture content of the meats in the top kettle constant within desired limits. With this type of moisture control and controlled kettle temperatures, it is possible to cook meats uniformly to a final optimum moisture content of 5.0 to 5.5% (at the former).

When meats are cooked to a lower moisture content, the material is crumbly and does not compact properly. There is high spillage from the edges of the formed cake and the meats do not "flow" in the press; this results in relatively poor expression of the oil.

When the meats are cooked to a higher moisture content, the material is too fluid in the press, which produces excessive "footing," with poor expression of oil. High-moisture cooked meats cause excessive strains within the press cloth during pressing, producing cloth rupture and consequent high press cloth costs.

(c) Temperature Control during Cooking. It is generally known by mill operators that the quality of cottonseed oil with respect to refining loss and color can be controlled in part by regulation of the cooking temperature. Thornton [7] and others have shown that it is desirable to heat the meats quickly in the top kettle to above 190° F. and then humidify the meats with hot water, to produce cottonseed oil with a low refining loss and a light color. Such oil has a relatively low phosphatide content.

Similarly, on high-moisture cottonseed meats. Fash [11] has shown that the evaporation of excess moisture in the meats is assisted by the use of open steam, either superheated or saturated, which is added to the top three kettles to raise the temperature quickly to above 212° F. This method of processing is reported to produce low-refining loss oil and meal of bright color.

To obtain a maximum yield of crude oil, which, however, is high in phosphatide content, it is generally known that lower top kettle temperatures are required, of the order of 170–180° F. The temperature in subsequent kettles is increased gradually to a final finishing temperature of 235° ± 5° F.

Figure 152 shows a typical five-high 84-inch cooker installation in a well-ordered press room. The cooker is well insulated to prevent excessive heat loss and heating of the press room. Each kettle is equipped with steam pressure control valves, automatic steam traps, and also steam pressure and temperature gages, both indicating and recording. It should be noted

[11] R. H. Fash, *Oil & Soap,* **10,** 125–126 (1933).

also that there is a cast iron vent pipe connected to the second, fourth, and fifth kettles, with adjustable vents for removal of moisture. A draft up the stack is maintained by means of either a fan or steam ejector, which is not shown.

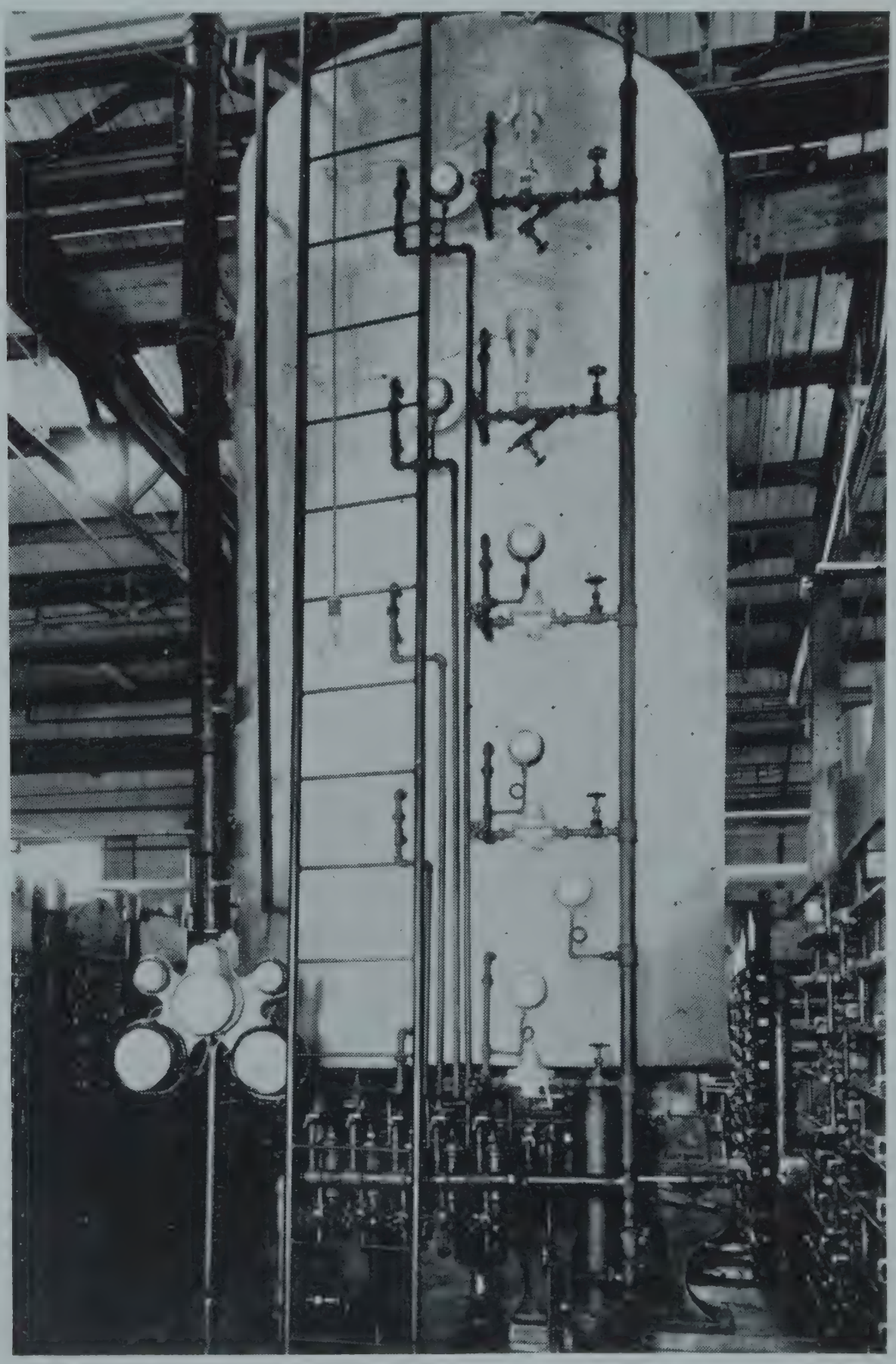


Fig. 152. Typical five-high cottonseed cooker installation.

This type of cooker has the capacity of processing the meats from 125 to 150 tons of cottonseed in 24 hours. By control of steam pressures, meats temperatures approximately as shown below are maintained in the kettles.

Kettle	Temperature, °F.
Top	175–195
Second	180–205
Third	200–215
Fourth	215–225
Fifth	225–235

Several process patents have been issued covering special methods of cooking cottonseed meats in stack cookers. One [12] embodies a sudden raising of the temperature in the top kettle by introducing hot steam into the incoming cold meats at a point near the bottom and adjacent to the outer wall of the top kettle. It is claimed that an oil is produced which is low in refining loss.

Another patent [13] claims the production of low-refining loss oil and a meal palatable in flavor and substantially free from toxic principles, which can be used safely for feeding animals and as a human food. In order to obtain these results, cottonseed meats are heated rapidly in the top kettle to 190° F. and humidified with water to bring the moisture content to 11–20%. The meats are then cooked at temperatures of 222° to 235° F., while the moisture content is reduced to 5.5–7.5%.

The acetone-insoluble material in the oil produced by this process is reported to be less than 0.50%.

(d) Cooking Time. The cooking time is determined by the height of meats carried in the various kettles (number of press loads), by the press charging schedule (which controls the drainage time in the presses), and by the daily tonnage of the mill.

Various investigators have indicated the desirability of cooking cottonseed meats thoroughly, but for as short a period as possible, in order to produce oil and meal having good color. It has been shown by Thornton [7] that increasing the cooking time, particularly when processing frostbitten or immature seed, results in the production of oil of higher refining loss.

In mill practice, the cooking time in stack cookers normally runs from about 80 to 120 minutes. This variation is due in part to processing the meats from 100 to 150 tons of cottonseed per day through the same 5-high cooker, in part to variations in the number of presses available. On prime meats, long cooking times are generally favored to improve oil recovery. On high-free fatty acid and damaged meats, a shorter cooking time is used to maintain the best possible meal color.

[12] J. P. Dickinson, U.S. Pat. 2,126,539 (1938).
[13] T. J. Harrell and C. W. McMath, U.S. Pat. 2,064,158 (1936).

4. Pressure Cooking

Much research and development work has been done at the Engineering Experiment Station, University of Tennessee, on the pressure cooking of cottonseed. This pilot plant work has been reported by various workers,[14] and the advantages of pressure cooking have been assessed in detail. As a result of the above development and also various independent contributions, a number of plant units have been installed and have been in operation for several years.

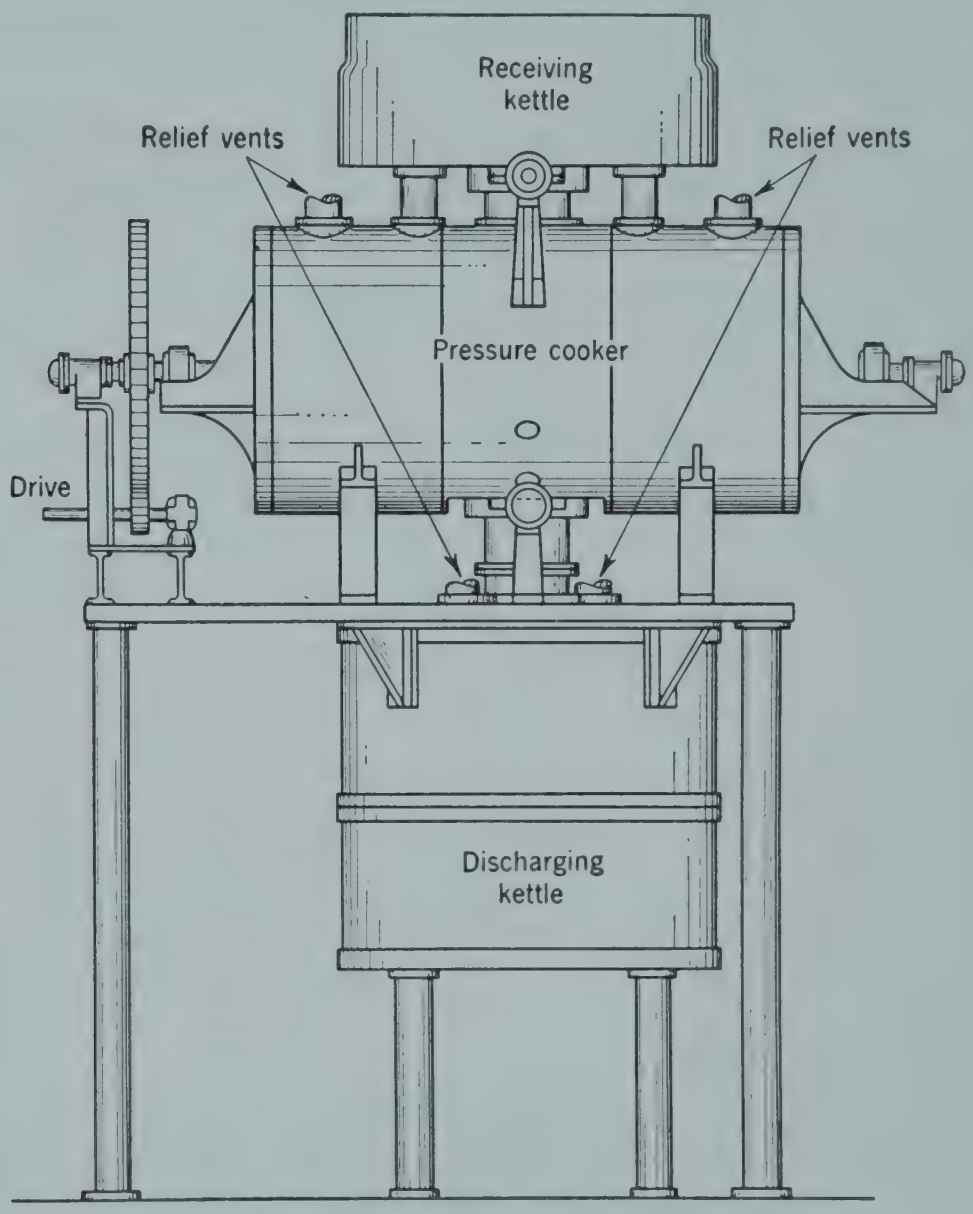


Fig. 153. Mill-size pressure cooker for cottonseed.

Figure 153 represents a sketch of a mill-size pressure cooker fabricated by The French Oil Mill Machinery Company. The unit is 10 feet long and 5 feet in diameter, and replaces the second and third kettles of a normal five-high cooker. The pressure vessel contains a hollow spiral-type agitator designed to mix and heat the meats thoroughly (with steam at 150 pounds pressure), and also to move the meats from the ends of the cooker to the center discharge port. The agitator is normally operated at 25 r.p.m., and clears the shell of the cooker by about $\frac{3}{16}$ inch.

[14] R. B. Taylor, *Oil Mill Gazetteer*, **42,** No. 7, 18–19 (1938), **42,** No. 8, 8–9, 18–20 (1938); *Chem. Met. Eng.*, **44,** 478–481 (1937). J. F. Leahy, *Oil Mill Gazetteer*, **42,** No. 11, 49–59 (1938). R. W. Morton, *Mech. Eng.*, **62,** 731–735 (1940).

The pressure vessel is operated batchwise in the following manner. From 4 to 6 press charges of meats are collected in the top kettle, which serves as a reservoir. The meats are dropped into the pressure vessel, the upper automatic hydraulically operated 18-inch valve is closed, and saturated steam controlled at 15 pounds gage pressure is turned on automatically. The meats are cooked at this steam pressure for 12 to 15 minutes, reaching a maximum temperature of 270° F. At the end of the cooking period, the pressure within the cooker is released automatically through a 6-inch relief valve and line connected to a cyclone. The lower hydraulic 18-inch gate is then opened automatically and the cooked meats are discharged into a kettle (corresponding to the fourth kettle of a 5-high cooker). Here additional moisture is vented off the hot meats, which then drop to the "fifth" or charging kettle. The above unit has a capacity for processing the meats from 100 to 125 tons of cottonseed in 24 hours. It will process satisfactorily meats up to 12% in moisture content. It is necessary to either dry high-moisture seed before pressure cooking or lower the capacity of the pressure cooker. At a 13–14% moisture content in the meats, the capacity is about 100 tons per 24 hours.

The actual pressure cooking cycle is short—12 to 15 minutes—but the temperature reached is high—260° to 270° F.—hence, with vigorous agitation with a steam-heated agitator, the cooking is thorough.

As a result of the effective uniform cooking, subsequent hydraulic pressing is reported to normally produce considerably higher crude oil yields. With a drainage cycle of about 45 minutes, the increased yield of oil is about 5 pounds per ton of seed, plus an additional phospholipid yield. The normal phospholipid content of stack cooker hydraulic oil, produced from prime seed, is of the order of 1.4–1.8%. Pressure-cooked oil from similar seed normally contains about 3.0 to 3.5% phospholipids. This increased content of emulsifying material results in higher refining losses; also it produces crude oil settling problems at the mill. Should the crude oil contain a slight amount of moisture for any reason, the phospholipid material will precipitate, increasing the settlings. The reworking of this settled material of jellylike consistency can be a considerable problem.

The color of pressure-cooled refined oil is normally equal to that of stack-cooked oil. The quality of the pressure-cooked meal with respect to color and free gossypol content is normally equal to that of corresponding stack-cooked meal.

5. The Skipin Process

Russian engineers [15] of the former North Caucasus Fat and Oil Trust and of the All-Russian Research Institute have developed, after years of

[15] A. I. Skipin, *Vsesoyuz. Nauch. Issledovatel. Inst. Zhirov,* **1935,** 40; *Masloboino Zhirovoe Delo,* **12,** 379–381 (1936). A. M. Goldovskii, *Fettchem. Umschau,* **43,** 21–26 (1936). Robert Heublyum, *Margarine Ind.,* **28,** 99–101 (1935).

preliminary work, a novel method of recovery of oil from various oil seeds. The process is based on definite control of the moisture content and temperature to which the flaked meats are heated in a specially constructed "precooker." The method is used particularly on oilseeds high in oil content, in which it is customary to "pre-press" the material, *e.g.*, sunflower, peanut, sesame, flax, castor, and cottonseed.

The Skipin process involves three successive operations: (*1*) moistening the meats with the requisite amount of water to release the oil, followed by heating the meats to free the oil from binding forces; (*2*) allowing the freed oil to drain through the screened bottom of the heating kettle; and (*3*) drying or cooking the partially defatted meats to a moisture content which permits subsequent hydraulic pressing.

A theoretical explanation of the Skipin process has been developed by Goldovskii, which is briefly the following. Oil and water each can wet the surface of meats particles, but they differ markedly in their affinity for the hydrophilic surfaces. Oil has little affinity for these surfaces, but water wets them because of its polarity and because it is adsorbed as the result of the activity of hydrophilic gels. Therefore, the surface tension of the meats particles at the water interface is insignificant, while at the oil interface it is considerable.

It has been shown that particles are wetted selectively by that liquid which has the lowest surface tension at the interface. Hence water will tend to displace the oil from the meats surfaces. At a certain moisture content, all the forces will be saturated by water, and the oil, then freed of molecular polar forces, will flow away readily. If the moisture content is too high, the oil flow stops, possibly because the structure of the finely divided meats has been altered (high aggregation).

The temperature of the meats is increased to reduce the viscosity of the oil. This is done by indirect heating of the meats with superheated steam; the temperature, however, must be carefully controlled in order to minimize denaturization of the proteins.

At the right moisture and temperature, the individual oil droplets unite to form a continuous phase and flow freely through the screened bottom of the special kettle. In the case of cottonseed meats, the moisture content of the meats in the Skipin kettle must be from 14.5 to 20% and the temperature 158° ± 3° F. The oil runs off from the special screen-bottom kettle in about 25–30 minutes. The partially defatted meats are then transferred to another cooker where the meats are dried to permit hydraulic pressing. The cooking (drying) of the meats requires from 96 to 112 minutes.

The advantages of the Skipin process are reported to be as follows. (*a*) The free gossypol is removed with the oil obtained in the special kettle. Hence the press cake contains practically no free gossypol. (*b*) There is a greater oil recovery. (*c*) The "free" oil is of good quality and refines easily.

The reported yield data are not impressive—in the case of cottonseed the fat content of the final press cake is said to be from 6.0 to 6.8%. This is poor press room work by United States standards.

D. Forming the Cooked Meats

In Figure 154 is shown a typical cake former for hydraulic box presses. Cooked meats at a temperature of about 230° F. and a moisture content of about 5.0 to 5.5% are formed into cakes between press cloth. The operation is performed as follows.

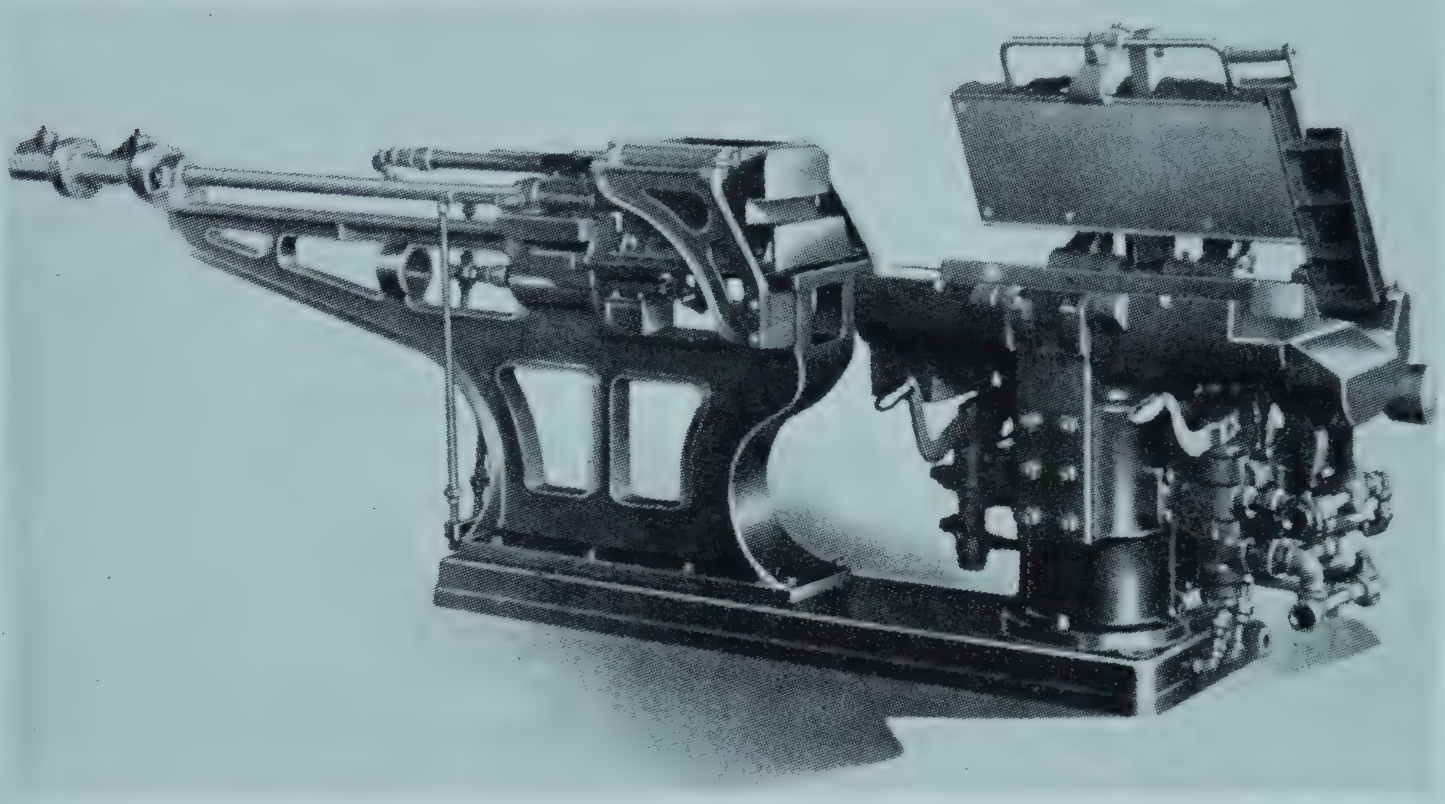


Fig. 154. Hydraulic cottonseed cake former. (Courtesy *The French Oil Mill Machinery Co.*)

(*a*) A press cloth made of human hair, wool, or other similar material, normally 66 inches long by 13½ inches wide is placed centrally in the bed of the cake former. (*b*) A hydraulic operated "buggy" deposits a uniform 3-inch deep layer of cooked meats on the cloth in the bed of the former. (*c*) The ends of the press cloth are lapped over the meats by the operator and the meats are then compressed hydraulically in the former to produce a compact cake enclosed in press cloth.

Each cake usually contains about 22 to 24 pounds of cooked meats and is removed from the cake former by slipping a flat "pan" under the compact cake. The cake is carried by the "pan shover" and placed in the boxes of the hydraulic presses.

Forming cottonseed meats is an important press room operation. Unless it is done properly, good expression results will not be obtained. The following instructions comprise important items which should be checked regularly by the press room supervision:

1. Form cakes of uniform density and thickness over the *full length* of the cake.

2. Clean the former bed (corners) and buggy at regular intervals (after each charging cycle) to produce firm-edged and full-depth cakes.

3. Compress cake tightly to reduce spillage and to obtain easier press loading.

4. Maintain press cloth in good repair. Remove broken cloths promptly. Well-formed cake cannot be obtained with ragged press cloths.

5. Maintain cake former in good repair—worn side plates make it difficult to remove compressed cakes from the former bed, resulting in high spillage and crumbled cake edges; this causes oil spots in the cake.

E. Press Cloths

In hydraulic box press operation, the oil flows from the pressed cooked meats through the cloth into the grooves or channels in the press mats. The cloth serves two purposes: it acts as a crude strainer or filter for the expressed oil, and it provides a ready means for transporting meats to and from the presses.

Human hair cloth has been the standard press cloth in cottonseed processing in the United States for many years. Many other types of press cloth made from various fibers—cotton, camel's hair, horse hair, various wools, and mixtures of these fibers—have been tested with varying degrees of success. During World War II a satisfactory wool cloth was developed and found to give good service. Metal cloth and metal mats made for cage presses have also been used effectively. Cloth of varying weaves and with different strengths in the warp and woof have been tested to determine the most economical material with respect to cloth cost and oil left in the cake. Each type of oil seed requires its specific type of press cloth. For cottonseed, the usual human hair cloth has a breaking strength of 1,000 pounds in the woof and 2,800 pounds in the warp.

Press cloth usage is an important item of cost in a press room. With good operation and proper repair of worn cloth, the usage is of the order of ⅓ pound per ton of cottonseed processed. As indicated above, thorough cooking and *uniform* moisture control are the important factors in insuring efficient usage of press cloth. Wet cooked meats are very destructive to press cloth, due to the generation of excessive strains as the result of "crawling" of the meats within the cloth. Torn cloths should be removed from service promptly and repaired.

F. Hydraulic Pressing

1. Design of the Press

About 95% of the cottonseed processing in the United States is done with hydraulic presses of the type shown in Figure 155. The press base contains a hollow cylinder about 14 inches in diameter carrying a ram

which raises the press boxes against the top "head." The head is supported by four steel columns and four heavy nuts hold it against the hydraulic pressure exerted by the ram. A typical press contains 15 boxes or spaces for the formed cake. The construction of the boxes is shown in Figure 156. In this figure the corrugations and oil grooves for removing the oil pressed through the press cloth from the press may be clearly seen.

In mill operation the angle-iron sides of the boxes are often inadvertently spread, allowing a portion of the cake to be pressed out beyond the width of the press cloth to form an oily

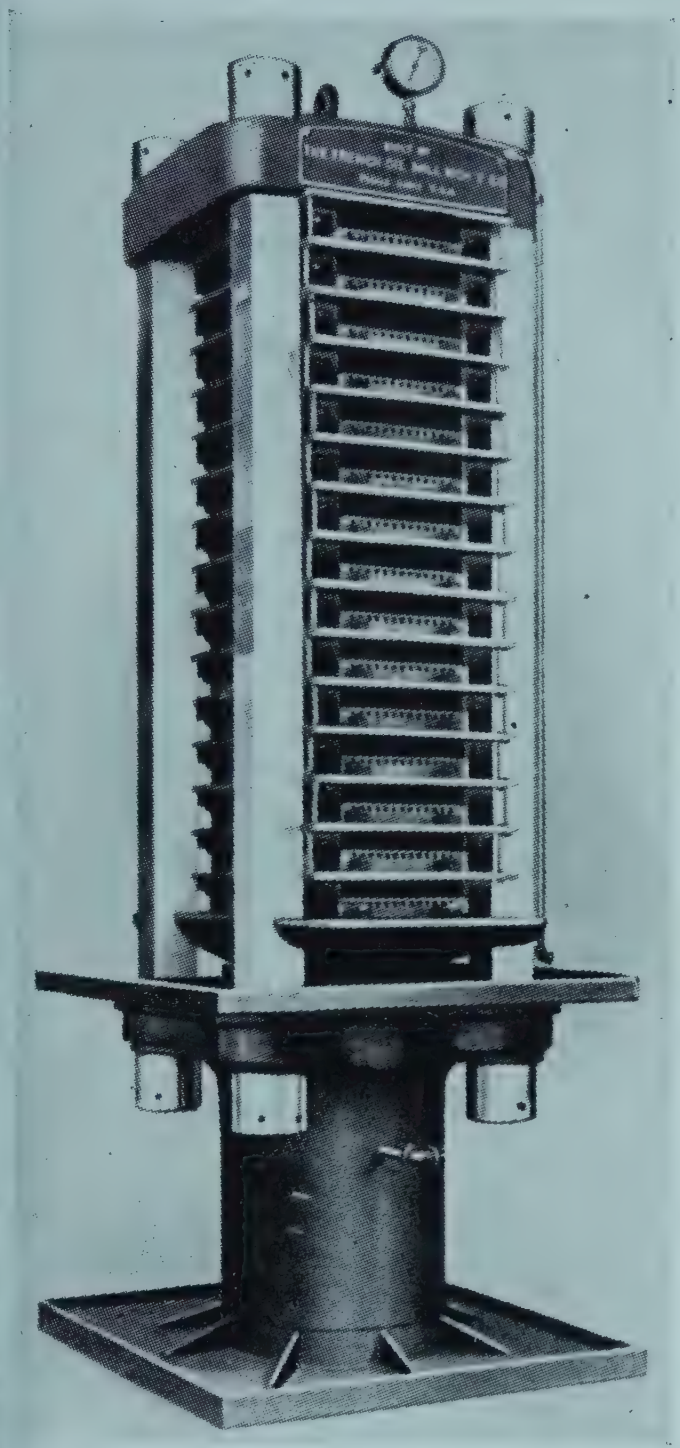


Fig. 155. Hydraulic box press. (Courtesy *The French Oil Mill Machinery Co.*)



Fig. 156. Construction of boxes for hydraulic press. (Courtesy *The French Oil Mill Machinery Co.*)

ridge along the sides of the cakes. This condition increases the oil in the cake considerably and can be corrected only by repair or straightening of the boxes.

The press is filled with 15 formed cakes by hand, as previously described. When 14 cakes have been placed in the press, the operator opens a valve which admits low-pressure oil to the press, raising the boxes. The last, top cake is placed in the press while the lower boxes of the press are rising.

2. Application of Pressure

It is desirable to take up the slack quickly in a press, to the point where the first oil begins to flow from the cakes. From that point on, the rate of rise of the press should be controlled in order to obtain optimum flow or drainage of oil from the cakes. If the pressure is applied too rapidly, the meats are compressed in such a manner as to block proper drainage.[16]

(a) Hydraulic System. In order to obtain a rapid initial press rise, hydraulic accumulator systems of the type shown in Figure 157 are in-

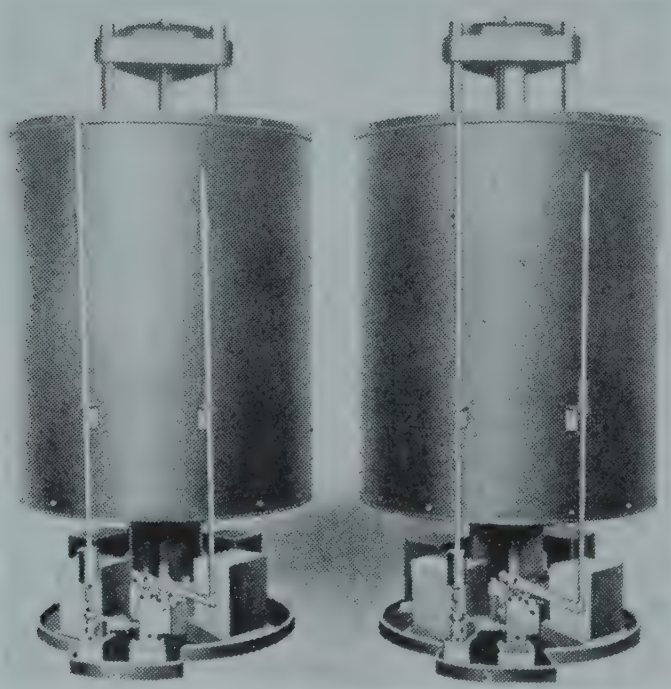


Fig. 157. Accumulators for hydraulic system. (Figs. 157, 158, courtesy *The French Oil Mill Machinery Co.*)

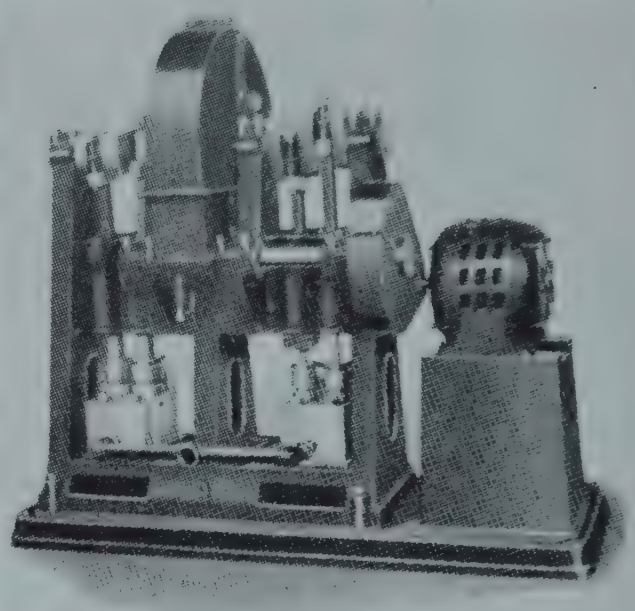


Fig. 158. A hydraulic pump of the four-throw, four-plunger, direct motor driven type.

stalled. The two functions of any accumulator are storage of a quantity of oil under pressure and the control or governing of the pump and pumping pressure. The accumulators keep a constant pressure on the presses and prevent the pressure from accidentally rising above a fixed maximum and thus bursting a cylinder. Two accumulators are normally installed, one for low pressure up to about 500 pounds per square inch gage and the other for high pressure up to about 5,000 pounds gage. Hydraulic pressure is supplied by pumps of the design shown in Figure 158. Hydraulic pressure on the presses is controlled automatically by change valves similar to that shown in Figure 159.

Another type of automatic hydraulic pumping system used in many mills consists of a combination high- and low-pressure pump (Fig. 160), a low-pressure accumulator, and valves for admitting and releasing the oil to the presses. No high-pressure accumulator or change valves are used.

[16] W. R. Woolrich and E. L. Carpenter, *Mechanical Processing of Cottonseed.* Eng. Expt. Sta., Univ. Tenn., Knoxville, 1935, p. 91.

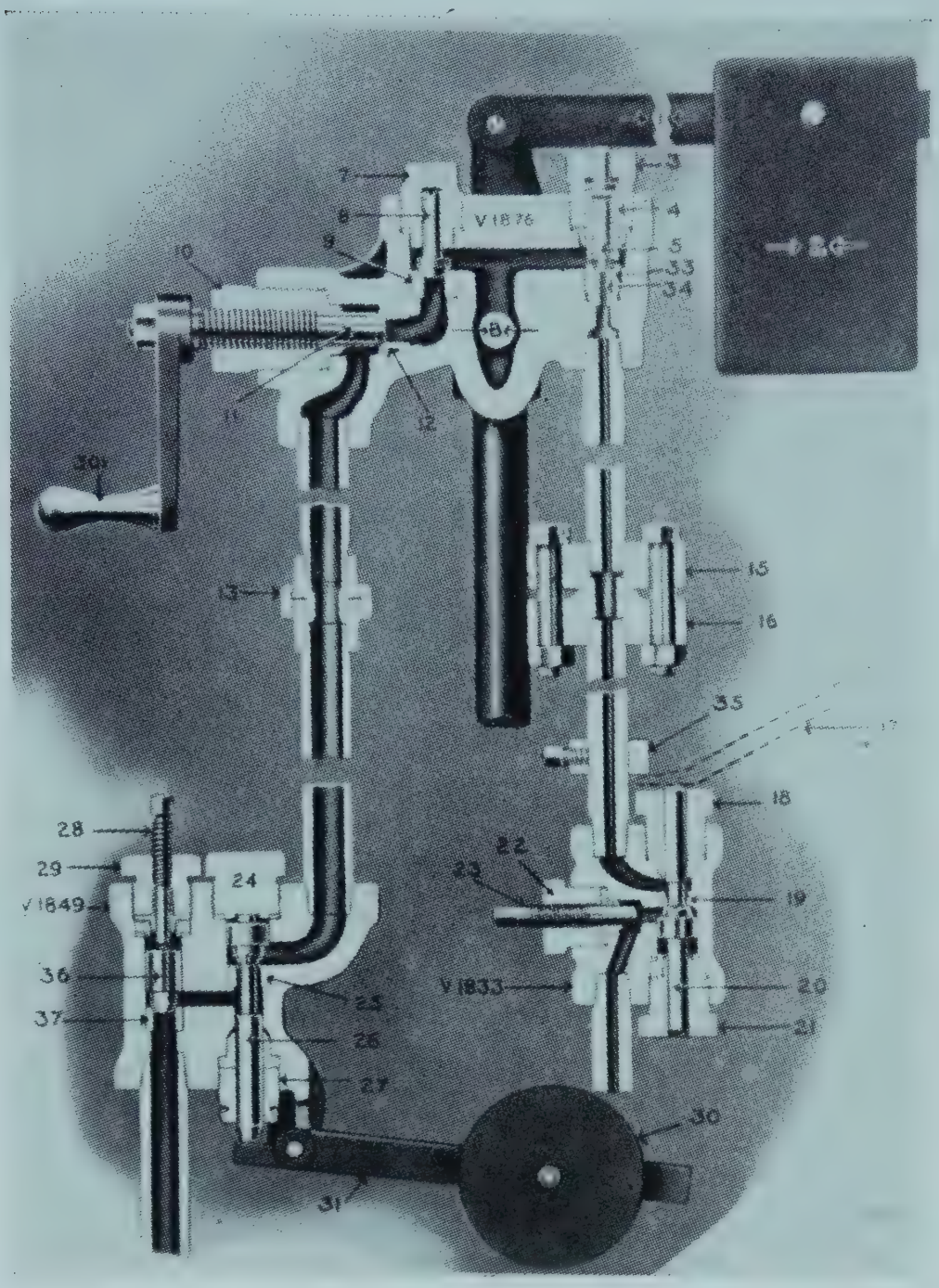


Fig. 159. Cross section of automatic hydraulic change valve.
(Courtesy *The French Oil Mill Machinery Co.*)

Change-Valve Body, V1876

1. Lever
2. Weight (large)
3. High-pressure check gland
4. Dashpot
5. High-pressure check
33. High-pressure check seat nut
34. High-pressure check seat
7. Low-pressure check gland
8. Low-pressure check
9. Low-pressure check seat
10. Screw-plug glands
11. Screw plugs
12. Screw-plug seats
13. 3/4-inch union, female, L.P.
14. 3/4-inch union, male, L.P.
15. 1/2-inch union, female, H.P.
16. 1/2-inch union, male, H.P.
301. Change-valve handle

High-Pressure Choker-Valve Body, V1833

17. Flushing lever
18. High-pressure choker gland
19. High-pressure choker seat
20. High-pressure choker stem
21. High-pressure choker gland
22. Stop gland
23. Stop stem
35. Flushing lever collar

Low-Pressure Choker-Valve Body, V1849

24. Low-pressure choker gland
25. Low-pressure choker seat
26. Low-pressure choker stem
27. Low-pressure choker gland
28. Stop stem
29. Stop gland
30. Low-pressure choker weight
31. Low-pressure choker lever
36. Low-pressure check
37. Low-pressure check seat

since the function of these is embodied in the pump. The low-pressure plungers of the pump have a constant fixed stroke, and together with the low-pressure accumulator give quick action in taking up the slack in the presses. The high-pressure plungers of the pump have a stroke controlled by double coil springs which gradually shortens as the pressure increases. The tension on the springs can be adjusted so that when the pressure on the press is 4,500 pounds the pressure in the pump cylinder will have forced the plunger back and compressed the springs to take the full travel of the crosshead. The plunger then remains stationary until the pressure is released. This type of hydraulic system operates with a lower power usage, as compared with the type described above, and is reported to also reduce the press cloth usage.

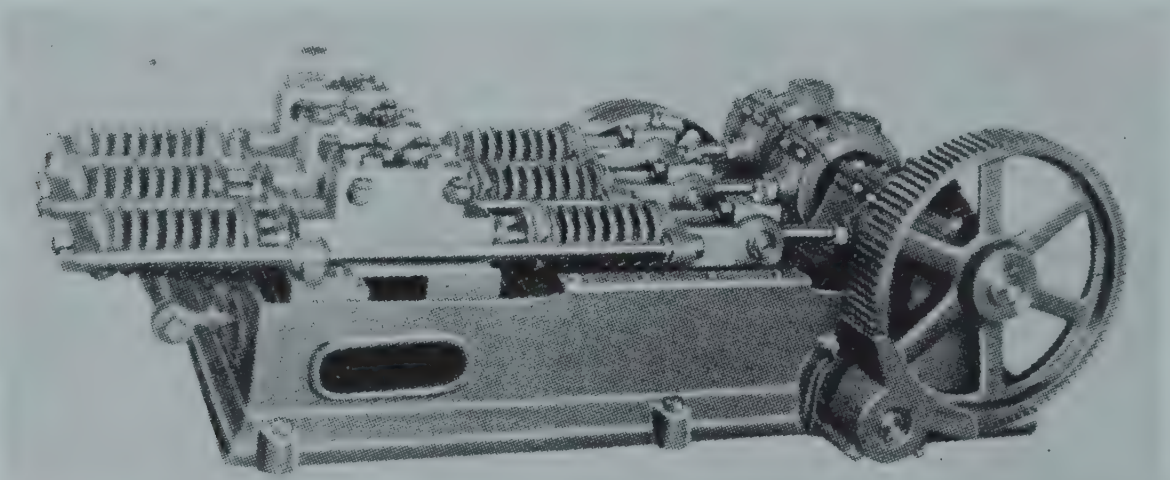


Fig. 160. Automatic hydraulic pump. (Courtesy *The Davidson-Kennedy Co.*)

(b) Rate of Application of Pressure. The rate of application of pressure on the presses varies considerably from mill to mill. This phase of press room control requires constant attention to maintain uniformity in press operation. At a desirable rate of increase of low pressure, the maximum low pressure will be attained in five to seven minutes from the time oil starts to flow from the cakes. The press is then brought up to full high pressure—about 2,000 pounds per square inch on the cake—as soon as possible.

(c) Drainage Time. A large proportion of the oil is pressed from the cakes at low pressure, if the pressure is applied slowly. The cakes are maintained under full high pressure for different lengths of time in various mills, depending on the number of presses available and the daily tonnage set for the mill.

The "drainage time" of a press may be considered to be the total "turnover time" minus about five minutes, since it normally takes about five minutes "down time" to empty and reload a press and raise it to the point where oil begins to flow from the cakes. With this as a basis, it is possible to calculate the approximate drainage time obtainable in an 8-

10-, or 16-press mill on any daily tonnage, if the following factors are known: (*a*) the number of press boxes, (*b*) the average net weight of cakes charged to the press (dry basis), (*c*) the percentage of hulls in the meats (normal percentage of meats in seed is about 55%, dry basis), and (*d*) the daily tonnage.

The following formulas may be used:

$$\text{turnover time, min.} = \frac{(0.284)\ (\text{total number of press boxes})\ (100 - \%\ \text{hulls in meats})}{(\text{tons per day})\ [100 - (\%\ \text{moisture} + \%\ \text{foreign matter in seed})]}$$

$$\text{drainage time} = \text{turnover time minus about 5 minutes}$$

Typical drainage time–tonnage data with 8, 12, and 16 presses (15 boxes each) in a mill are shown below (in terms of average drainage time).

Tons per 24 hrs.	Drainage time, minutes		
	8 presses	12 presses	16 presses
50	64	98	—
100	29.5	46.5	64
150	18	29.5	41
200	12	21.0	29.5

An important factor in determining drainage time is the percentage of hulls in the meats. This is so for several reasons. A high content of hulls interferes with proper flaking of the meats. The presence of hulls also increases the volume of material to be handled by the presses, and consequently decreases the allowable drainage time. A ton of average prime cottonseed containing 11% moisture and 1% foreign matter will produce the following meats and hull loads per ton to the press room (each load is calculated on the basis of 11% moisture in the meats and hulls): 1,080 pounds pure meats, 1,150 pounds meats plus 5% hulls, 1,200 pounds meats plus 10% hulls, or 1,300 pounds meats plus 15% hulls. The undesirable effect of hulls in the meats on drainage time is obvious, particularly since it has been shown [17] that hulls do not produce a more "porous" cake with better oil drainage.

3. Drainage Time in Relation to Amount of Oil Left in Cake

There are many factors which need to be controlled in the experimental determination of a drainage curve for hydraulic pressing. Some of the more important of the necessary precautions will be mentioned to indicate the difficulties involved. The press room operation at each drainage time

[17] J. F. Leahy, *Oil Mill Gazetteer,* **45,** No. 4, 20 (1940).

must be normalized to obtain equilibrium press temperatures. Figure 161 shows the effect of temperature on the viscosity and fluidity (tendency of the oil to flow) of cottonseed oil. The effect of press temperature particularly at long drainage times is important. Many repeat results must be obtained, since cake sampling and reduction of samples even under the best conditions are difficult opera-

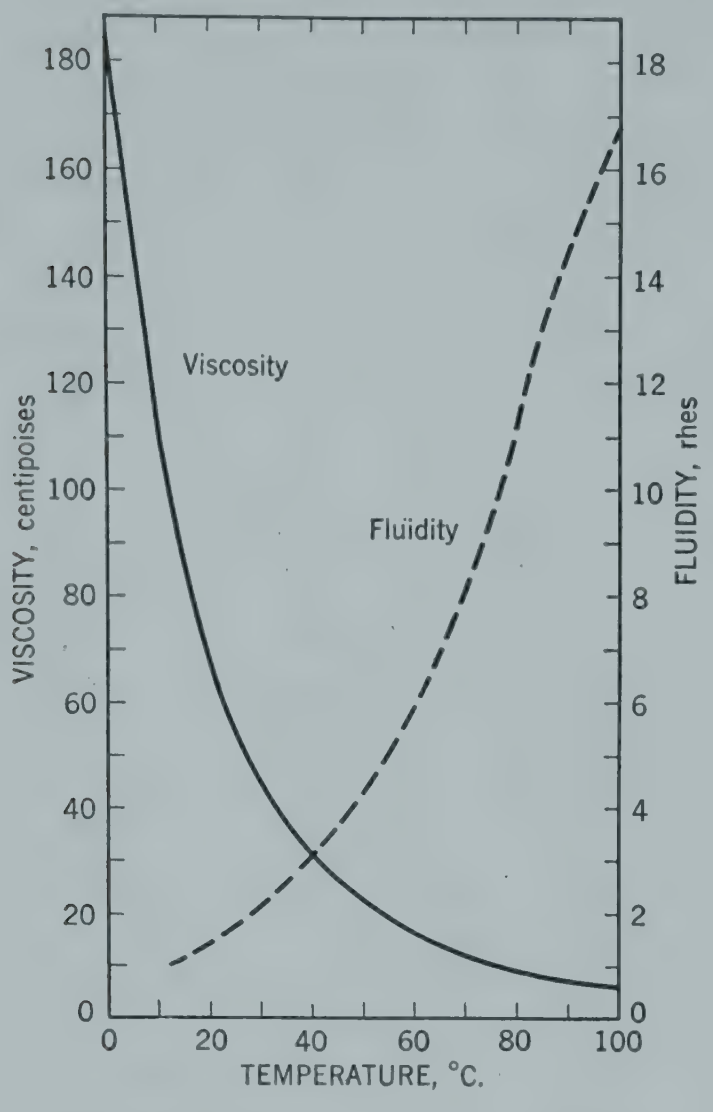


Fig. 161. Temperature *vs.* viscosity and fluidity of cottonseed oil.

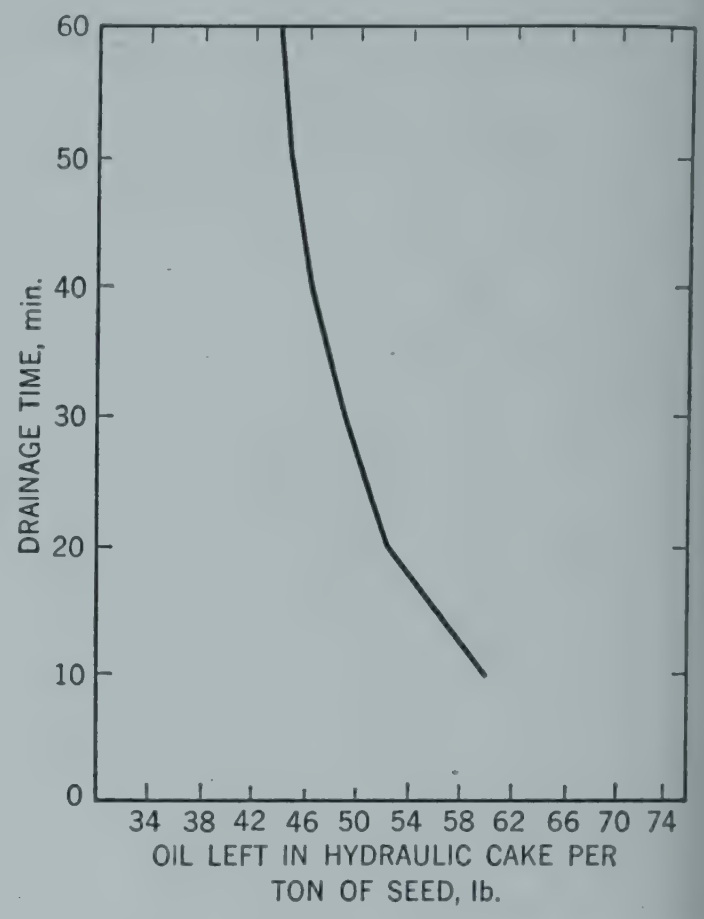


Fig. 162. Hydraulic press drainage curve, from mill data on prime cottonseed.

tions. Also, many other factors must be rigidly controlled, as for example, the proportion of hulls in the meats, the cooking conditions, and the moisture content of the seed. There must be a normal return of oil settlings, trimmings, and other rework fractions.

In Figure 162 is shown a typical average drainage curve for stack-cooked hydraulic box-pressed cottonseed cake. The slope is similar to that reported recently by Baskervill and Wamble [18] for the average of eight hydraulic mills and also for pilot plant pressure-cooked meats. These authors indicate that the present average pressing cycle in cotton oil mills in the United States is 30 minutes or less. They show also that it would be profitable to increase the pressing cycle to a minimum of 47 minutes and suggest that this could be attained by increasing the number of presses by about 50%.

[18] W. H. Baskervill and A. C. Wamble, *Oil Mill Gazetteer*, **50,** No. 2, 32 (1945); *Univ. Tenn. Eng. Expt. Sta. Bull.*, **No. 13** (1945).

TABLE 169

Excess Cottonseed Crushing Capacity in the United States

State	Average annual production of cottonseed 1936–1945, 1000 tons	Percentage of total production delivered to mills	Estimated crushing capacity, 1000 tons	Excess crushing capacity, 1000 tons	Number of mills
Alabama	429	80	857	588	30
Arizona	84	97	241	138	7
Arkansas	594	89	1,127	648	26
California	186	92	397	217	9
Florida	10	76	33	29	1
Georgia	412	82	1,423	1,146	45
Louisiana	284	84	632	428	19
Mississippi	765	87	1,517	940	41
Missouri	158	95	82	−64	3
New Mexico	48	92	75	22	3
North Carolina	262	87	885	679	36
Oklahoma	259	79	750	558	30
South Carolina	335	84	810	544	29
Tennessee	214	84	761	593	13
Texas	1,357	82	3,987	3,014	135
Virginia	12	85	0	−9	0
All others	8	85	50	41	1
Total	5,417	(*Av.*) 85	13,627	9,512	428

Table 169 shows the amount of cottonseed produced and delivered to the mills during the past 10 crop years (1936–1945), and also the number of mills operating in each state and the total crushing capacity and *excess crushing capacity*. Examination of these data suggests that perhaps additional hydraulic crushing equipment is not needed to attain the desirable objective of realizing a larger oil yield from the present United States

TABLE 170

Cottonseed Crushed at U.S. Mills in Different Months[a]

Month	Tons crushed	Percentage total crush	Cumulative percentage
August	130,457	3.0	3.0
September	489,449	11.2	14.2
October	689,294	15.7	29.9
November	657,947	15.0	44.9
December	571,629	13.0	57.9
January	532,138	12.1	70.0
February	523,271	9.7	79.7
March	346,577	7.9	87.6
April	227,041	5.2	92.8
May	151,889	3.5	96.3
June	93,620	2.1	98.4
July	68,748	1.6	100.0

[a] *Cotton Production and Distribution*, U.S. Bureau of the Census. Average figures for the 10-year period 1936–1945.

cottonseed crop. Instead, with the knowledge of how to store seed with little deterioration in storage, the *rate of crushing* at the mills could be reduced markedly to provide year-round mill operation. This can be done with good economy and would not only result in longer drainage times and larger oil yields, but would also contribute definitely to a sounder oil milling economy by providing steady employment for mill employees.

The crushing data in Table 170, for the crop years 1936–45, show the present seasonal nature of the cottonseed crushing industry and support the above point of view.

4. Importance of Continuous Operation

Perhaps the single most important factor in good press room performance is continuous uninterrupted operation. It takes several hours to normalize a cooker and set it for correct load, correct temperatures, and uniform moisture. If the flow of meats to the press room is interrupted for any reason, cooking becomes nonuniform and poor expression results inevitably follow.

A mill having frequent short "down times," due to mechanical failures which affect the flow of meats to the press room, can easily lose 5 pounds additional oil per ton, due to poor cooking control and subsequent poor oil expression.

5. Discharging Hydraulic Box Presses

It is important to maintain the cakes in the presses under full pressure as long as possible. Often there is a tendency for the "press knocker" to release the pressure from the presses earlier than is desirable, and it is not uncommon to see several presses "down" at one time. This is costly processing, as can be seen from the drainage curve. The ideal schedule, which can be maintained with proper supervision, is to have one press going down, another going up, and one being filled at all times.

The cakes are removed from the presses by means of a "knocker" from behind the presses or by means of a "hook" from the front. The former practice is the more desirable method, since it is definitely less destructive to the press cloth.

6. Stripping and Trimming the Cake

The cakes from the press are placed on a buggy and transported to the "stripper," where the cloths are stripped from the cake by means of a rotating "gooseneck" quill. A typical stripper is shown in Figure 163.

The stripped cakes are placed on an adjacent cake trimmer (Fig. 164). Each cake passes through this machine in such a manner that a set of rotating knives cuts simultaneously the soft edges from both ends of the cake. As the cakes pass through the trimmer, spring tension holds the

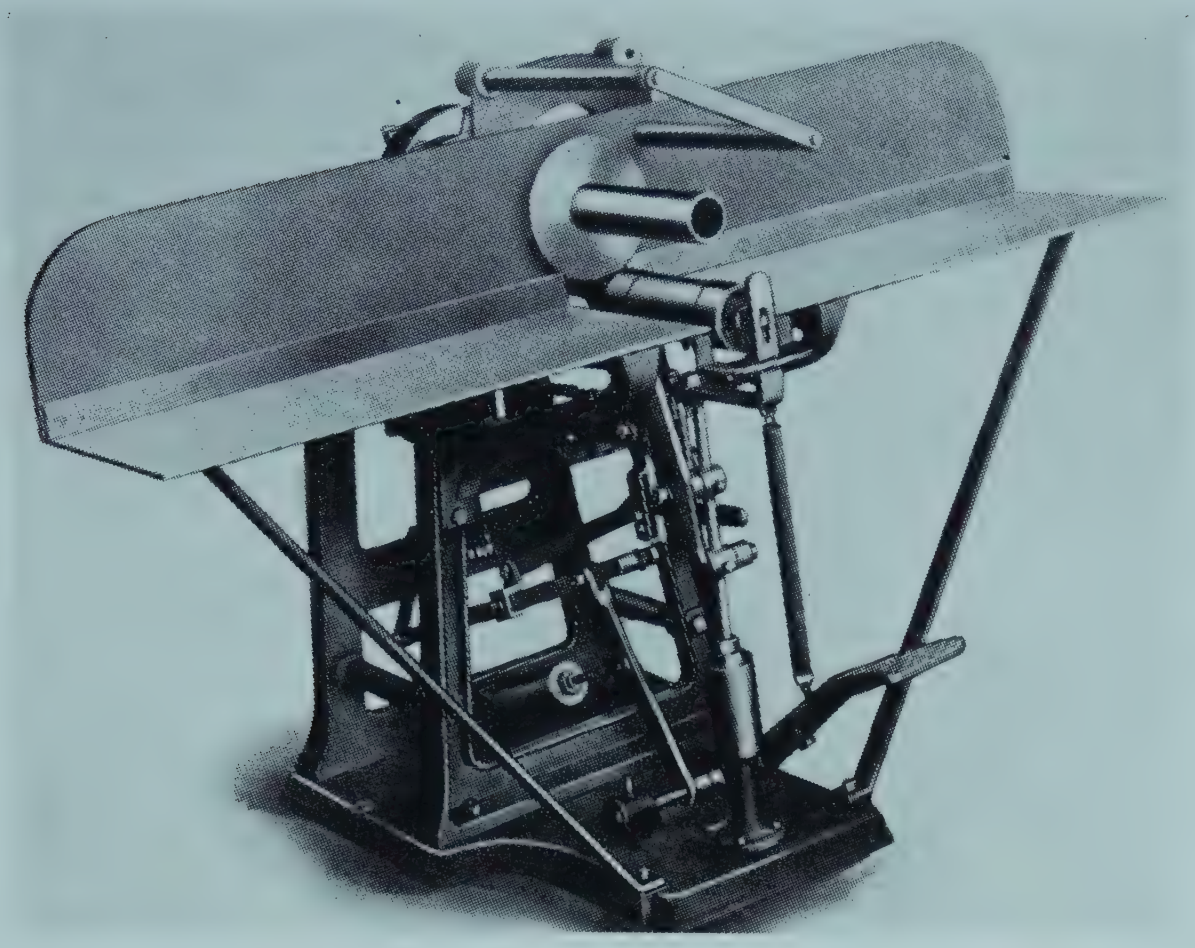


Fig. 163. Cottonseed cake stripper. (Courtesy *The French Oil Mill Machinery Co.*)

knives in contact with the ends of the cake. The tension is usually set to cut about ¼ inch of hard cake in addition to the soft oily ends of the cake.

The portion cut from the ends normally comprises about 6% of the total cake, and contains up to 10–14% oil. The trimmings are normally

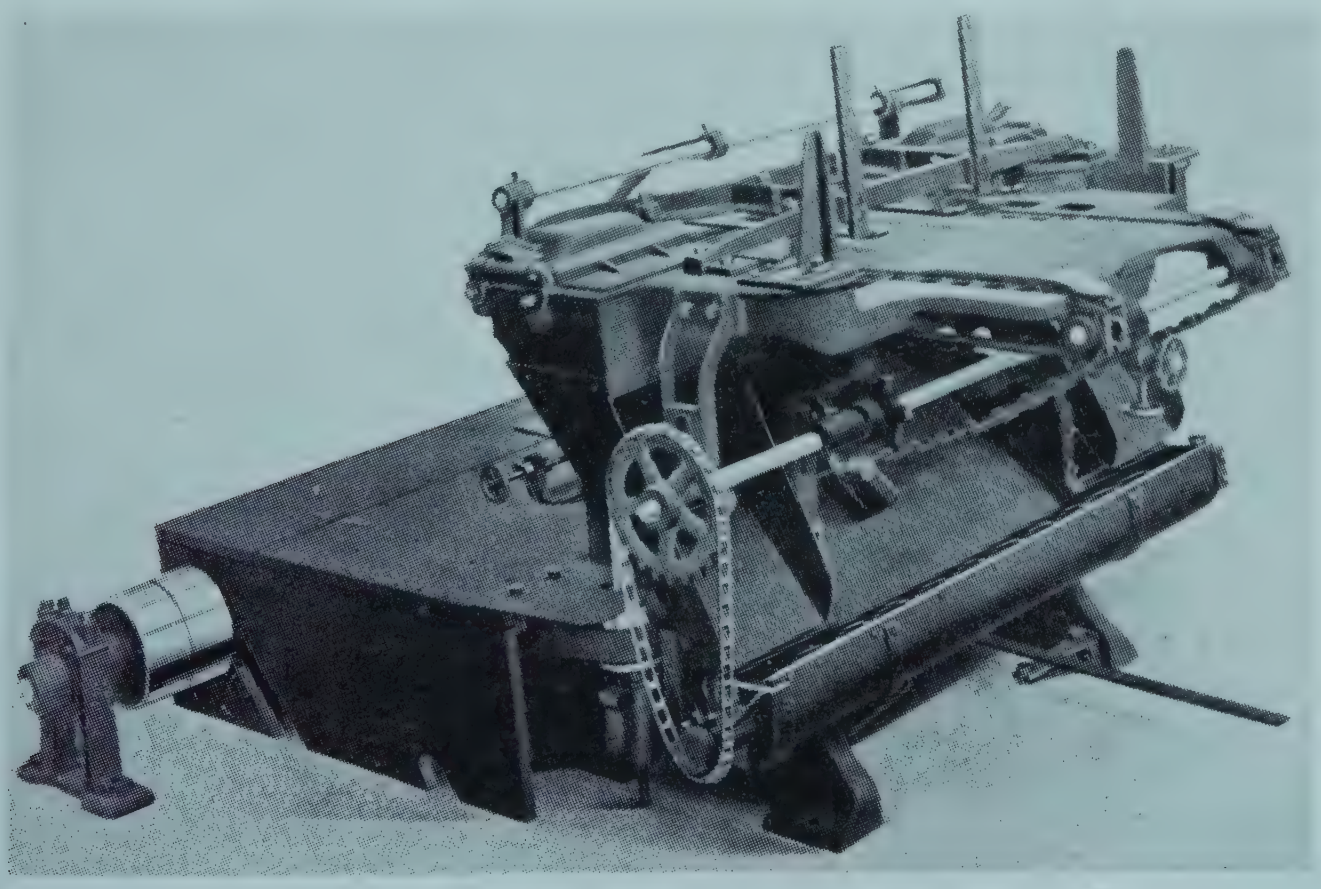


Fig. 164. Cottonseed cake trimmer. (Courtesy *The French Oil Mill Machinery Co.*)

blended continuously with other materials flowing to the cooker, fo reprocessing.

7. Settling of the Crude Oil

The crude oil, as it flows from the presses, is caught by the lower par of the press and directed into an oil trough back of the presses. Figure 152 (page 622) shows oil pans and trough behind the presses at the left of the photograph. The oil trough is usually about 14 inches deep and contains



Fig. 165. Continuous oil settling tank, top view.
(Courtesy *V. D. Anderson Co.*)

a stand pipe overflow, which permits settling out of meal fines in the trough. These meal fines are removed periodically, from once each shift to once each day.

The oil usually passes through a series of settling tanks located in the basement. The settled oil from the last tank is pumped either to outside oil storage tanks or to tank cars. The basement settling tanks are emptied

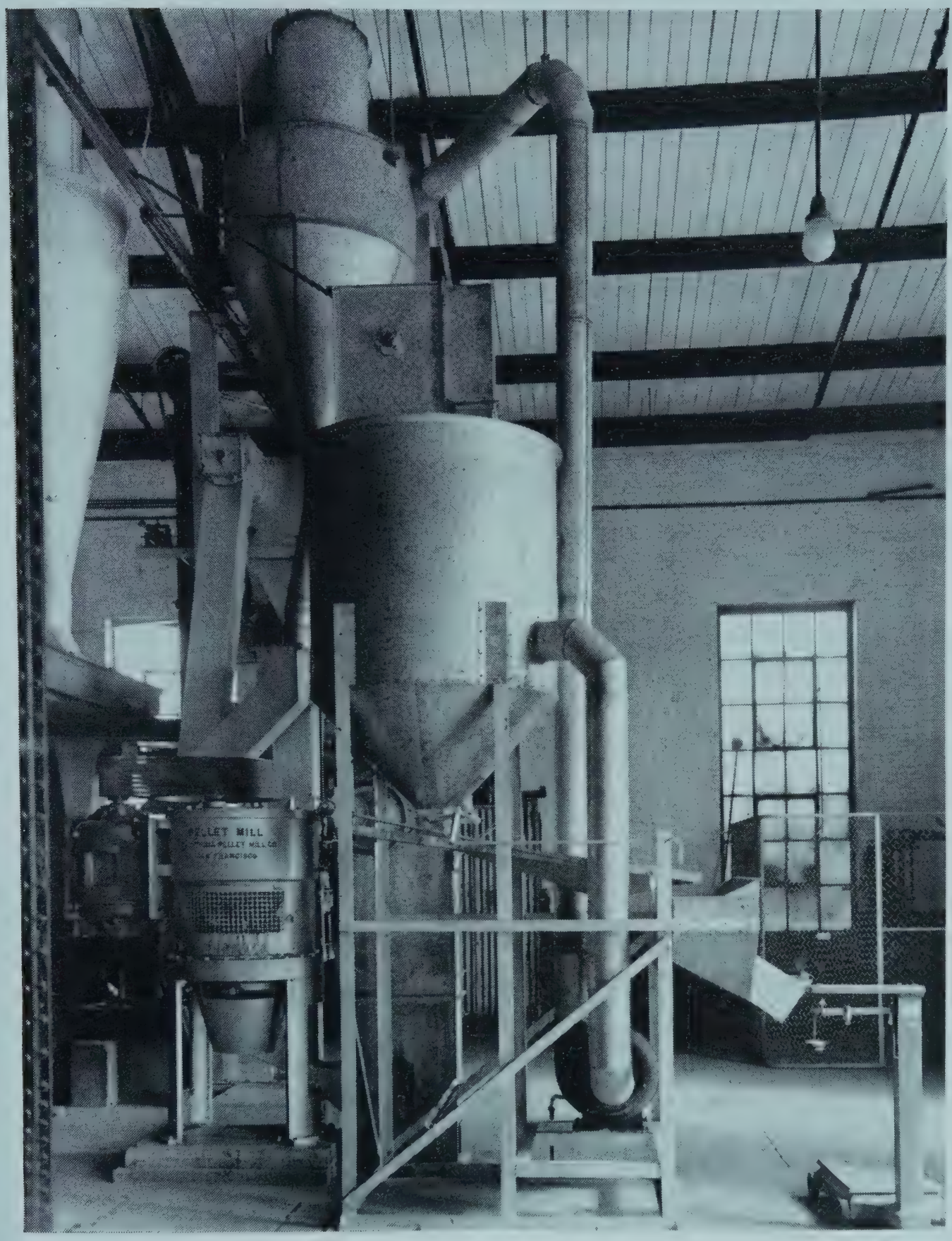


Fig. 166. Cottonseed meal pelleting machine.

in rotation by pumping off the oil through a "floating" suction and then removing the settled-out solids by hand. The settlings are normally mixed with other meal solids and reworked. This batch method of handling settlings has many objections.

The use of a continuously discharging oil settling tank (Fig. 165) has many advantages, such as lower labor costs, better removal of solids, continuous return of settlings to the press room (resulting in better oil recovery), and generally improved cleanliness.

The equipment can be installed so as to eliminate also the settling trough behind the presses and thus handle all of the press fines.

G. Processing of the Cake

The trimmed cake may be sold as slab cake or as cracked cake after passing through a cake cutter, or ground into meal which is sold on a protein basis, normally as 36, 41, or 43% protein cottonseed meal. Ground cottonseed hulls (hull bran) are added when necessary to adjust the protein content to the desired level.

The meal may be converted into various-sized pellets, of such size as to be particularly adapted to feeding various animals. For example, a cattle-size pellet is normally ¾ inch in diameter and about 1½ to 2 inches long. Pellets are particularly valued as a feed for animals on the range.

Pellets are produced by mechanically compressing hot meal of proper moisture content through dies. Figure 166 shows a typical pelleting machine.

H. Use of Cage Presses

Few cage presses are used for processing cottonseed meats in the United States. These presses are normally used on seeds or nuts containing more than 40% oil, since they prevent in a large measure the spreading and escaping of cooked meats from the sides of the cake under pressure, and thus reduce the amount of material to be reworked.

The cooked meats are retained in a cage or pressing chamber equipped with steel sidewall drainage plates having narrow slits and small perforations through which the oil can flow when the material is subjected to pressure. The advantages of a cage press are that the edges of the cake are hard and require very little, if any, trimming, and the amount of foots escaping with the oil is negligible.

A typical installation usually consists of a filling and a discharging press and a number of finishing presses where the oil expression takes place. A typical installation is depicted in Figure 167. The meats from the cooker are transferred to and uniformly distributed in the charging press by means of a distributor attached to the bottom of the cooker.

The removable cage, having been placed in proper position in the press, is filled in the following manner. The press ram is raised to its highest position. A steel mat and a press cloth is placed on the ram and the ram is lowered automatically about 3 inches, which is the normal thickness of a layer of meats for each cake. A charge of meats is deposited, the layer of meats is covered with a press cloth and another plate and cloth, and the ram is again lowered. In this manner, approximately 40 cakes are placed in the press. A special head block is pushed into position and pressure is admitted to the cylinder, causing the ram to rise and force the contents of the stationary cage into the movable cage. The movable cage is then transferred by means of a carriage to one of the finishing presses where the oil is expressed. After a definite drainage period, the cage is

transferred to a discharging press where the cakes are forced out of the cage by means of a press ram.

The efficiency of the cage press for pressing cottonseed meats, for the same drainage time, is about equal to that obtained in good box press operation.

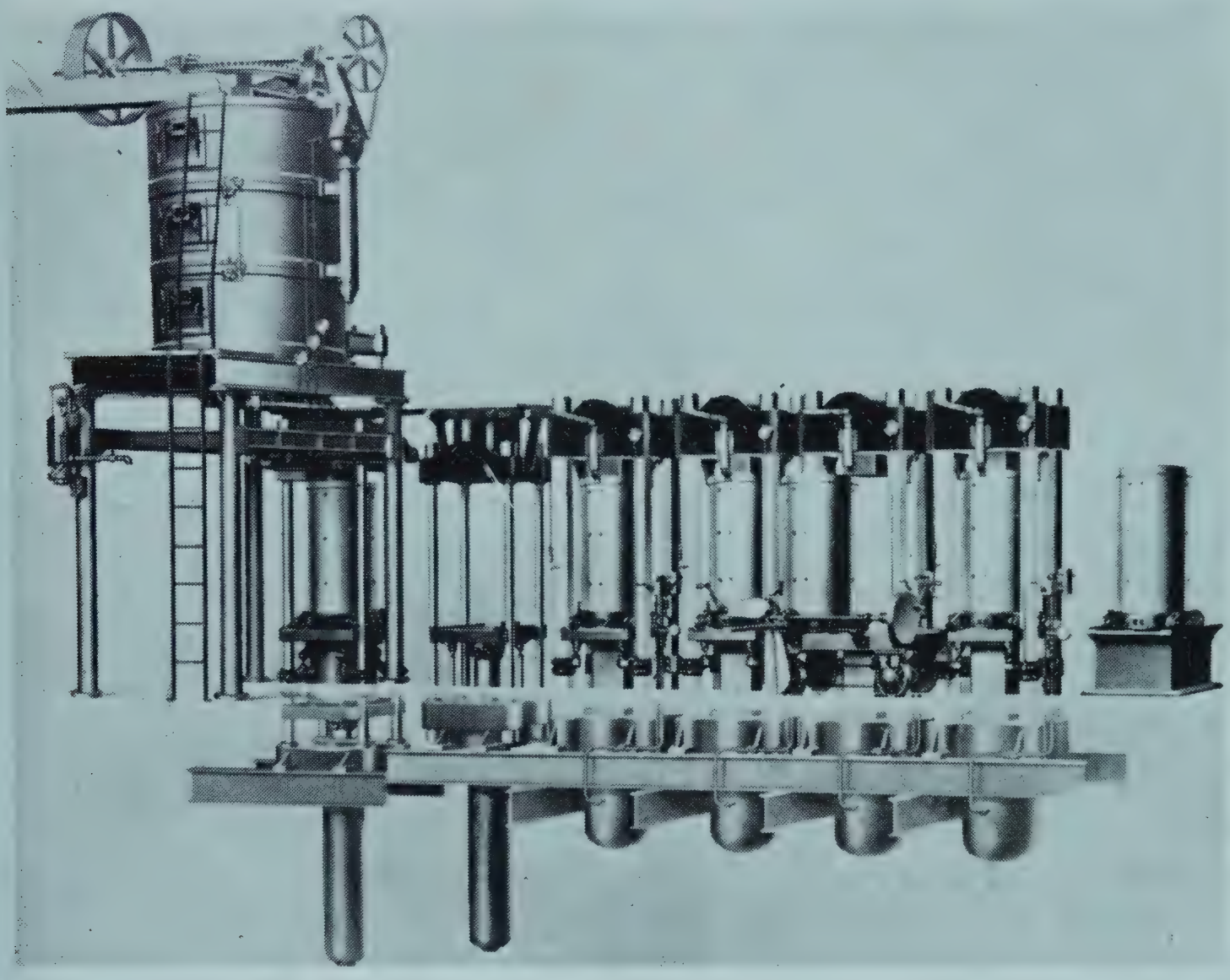


Fig. 167. Cage press installation. (Courtesy *The French Oil Mill Machinery Co.*)

III. Expeller Processing

The successful operation of expellers or screw presses for processing cottonseed meats has been discussed by Leahy[19] and others.[20] The reported advantage of processing cottonseed meats by means of expellers as compared with the more usual hydraulic presses are as follows: (*a*) There is a saving in labor in the press room. In a 100-ton per day mill, three operators replace the normal press room crew of 21 men. (*b*) Increased press room efficiency is obtained. An expeller "standard" of 48 is achieved, compared with an average hydraulic standard of about 65. This is equivalent to an increased oil yield of 11 to 12 pounds per ton of cottonseed.

[19] J. F. Leahy, *Southern Power and Ind.*, **57**, No. 10, 37–44 (1939).

[20] M. K. Thornton, Jr., *Oil Mill Gazetteer*, **37**, No. 1, 26–28 (1932). Anonymous, *The Expeller Press*, **6** (April, 1943). C. B. Upton, U.S. Pat. 2,262,566 (1941). R. T. Anderson (to V. D. Anderson Co.), U.S. Pats. 2,065,848 (1936), 2,269,898 (1942), 2,275,337 (1942), and 2,299,784 (1942).

("Standard" = per cent oil in cake divided by per cent ammonia in cake.) The oil is equal in quality to hydraulic oil. (*c*) Nontoxic cottonseed meal is produced. The meal is very low in free gossypol content. (*d*) The cost of press cloth is eliminated.

Expeller processing requires considerably more power than hydraulic processing; each cooker-expeller unit uses about 60 h.p. and has a capacity of about 23 tons of cottonseed per 24 hours.

Figure 168 shows a 4–36 inch cooker-expeller installation for processing

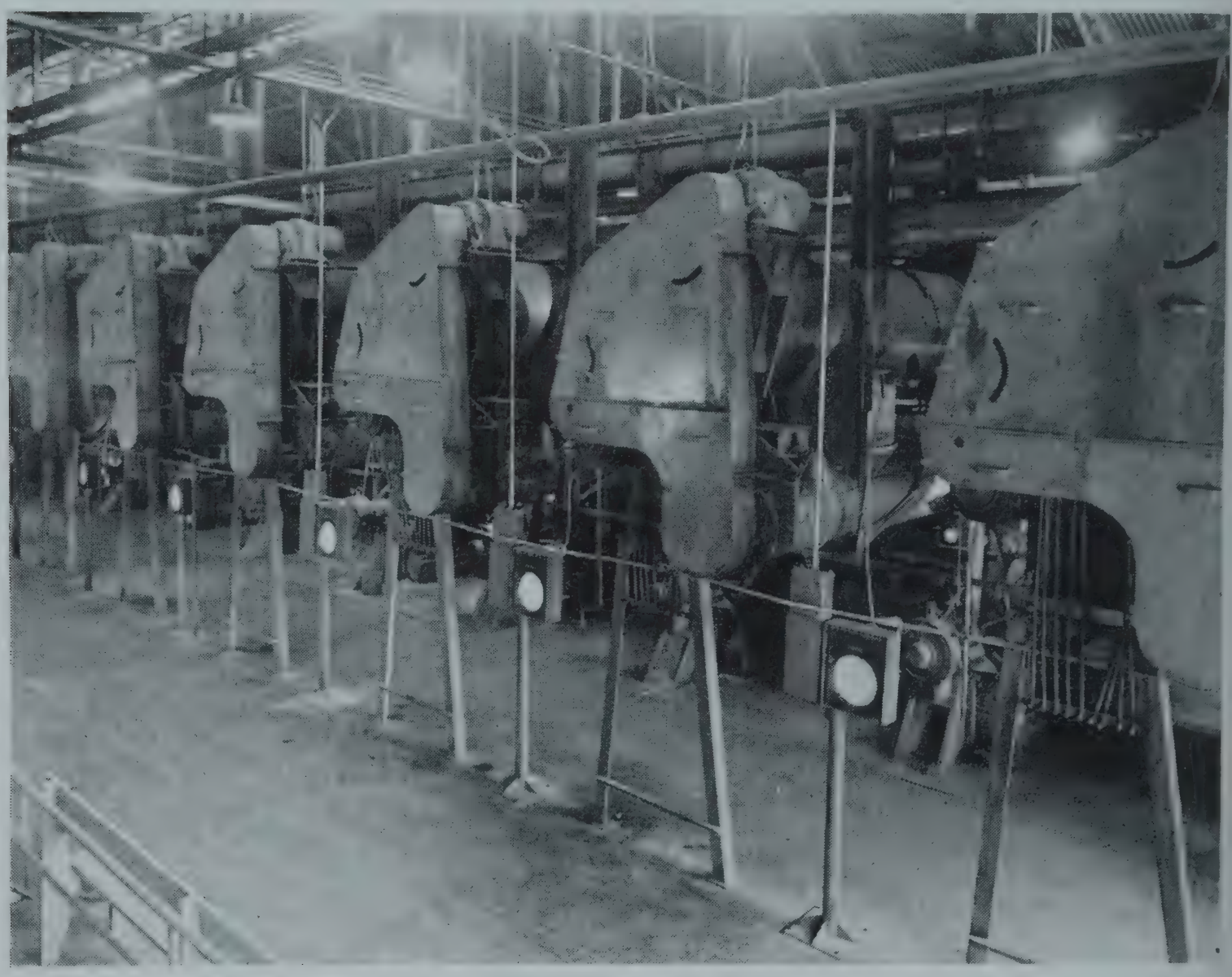


Fig. 168. Cottonseed expeller mill. (Courtesy *Producers' Cotton Oil Co.*)

cottonseed meats. Briefly, the processing of hulled meats is carried out in the following manner. The meats are flaked through the conventional 5-high roll, and the flaked material is mixed continuously with a proportional amount of filter press muds (from filtering the oil) and settlings from the oil settling tank. This mixture is passed by a magnet to remove any tramp iron and then conveyed into the 36-inch cylindrical cooker and subsequent final conditioner. The meats are cooked and dried at a maximum temperature of about 240° F., so that the material entering the vertical expeller has a moisture content of 3.0 to 3.5%. The type of expeller shown in Figure 168 has a capacity equivalent to the meats from about 23 tons of cottonseed per 24 hours.

The application of pressure cooking prior to expelling has been reported to show promise [21] and has been used successfully in commercial operation. More recent developments favor the use of the cooker-conditioner unit described above for cooking and drying cottonseed meats before expelling. The capacity of this unit operating at atmospheric pressure is adequate for reducing the moisture in meats containing up to 12% moisture.

As the meats pass through the expeller, considerable pressure is developed (up to 10–12 tons per square inch) and the expressed cake contains about 4.0 to 4.5% oil. The frictional heat developed during pressing is removed by circulating continuously about 35 to 40 gallons per minute of cooled settled oil over the expeller barrels. This also removes, as produced, any fines extruded through the barrel spacings. These openings vary in size from 0.010 to 0.040 inch in different sections of the vertical and horizontal barrels.

The oil expressed from the meats, together with the cooling oil, passes on to a continuously discharging oil settling tank (shown in Fig. 165). The meal settlings are discharged continuously and returned to the expeller feed. A portion of the settled oil is passed through a heat exchanger and cooled to about 150° F. and circulated over the expeller barrels. The excess settled oil is filtered before passing on to oil storage.

The hot expeller cake may be cooled before or after grinding, with humidification, in a cake or meal cooler. The material may be stored in bulk or sacked.

Typical cooker-expeller processing results on hulled cottonseed meats are reported to be as follows. Capacity per expeller per 24 hours: 22–24 tons whole cottonseed. Analysis of cake: moisture, 2.75%; oil, 4.04%; ammonia, 8.41%. Press room standard, 48. Refining loss of filtered oil: 3.0 to 4.0%.

The estimated amount of cottonseed now annually processed by continuous expeller and screw press operation is less than 200,000 tons.

IV. Solvent Extraction

A. Experimental Work. Basic Considerations

Much work has been done on the problem of extracting the oil from cottonseed meats by means of solvents. Wesson [22] stated a number of years ago that solvents had not been used on cottonseed, because with improper methods and lack of knowledge it had been impossible to obtain refinable oils. More recently (1941), it has been stated [23] that solvent

[21] J. F. Leahy, *Oil Mill Gazetteer,* **45,** No. 4, 20–24 (1940); *Southern Power and Ind.,* **57,** No. 10, 37–44 (1939). R. W. Morton, *Mech. Eng.,* **62,** 731–735 (1940). A. P. Holly, *Cotton and Cotton Oil Press,* **40,** No. 12, 9, 20 (1939).

[22] D. Wesson, *Oil & Fat. Ind.,* **7,** 258 (1930).

[23] J. F. Leahy, *Southern Power and Ind.,* **59,** No. 1, 44–48 (1941).

extraction appears to be more successful when applied to soybeans and linseed than to cottonseed.

Examination of the development work reported from many laboratories and a review of the patent literature shows that many investigators have been concerned with obtaining an extracted oil of suitable color. For example,[24] cottonseed meats have been treated with 80% alcohol to extract the coloring matter with relatively little oil; the meats were then subsequently extracted with a hydrocarbon to recover the oil. Others have extracted cottonseed meats with mixtures of hydrocarbons and ether,[25] benzene and alcohol,[26] and propane and butane [27]—all to obtain lighter colored extracted oils.

The difficulty lies in that the coloring matter in the resin glands is extracted by many solvents as effectively as is the oil. The crude oil obtained in some cases is, therefore, much darker than normal hydraulic-pressed cottonseed oil. In fact, in many instances, it is almost black in color and cannot be refined to produce a light colored refined oil.

Some solvents have been found to extract the oil from cottonseed meats more effectively than others. Benzene is reported to be a more efficient solvent for extracting cottonseed oil, than benzine,[28] but it is known to extract very much more coloring matter. This is also true of diethyl ether and dichloroethane, which effectively extract gossypol to produce a meal having excellent feeding value.[29]

Another investigator [30] has found that increased extracted oil yields can be obtained by drying cottonseed meats to a low-moisture level and then extracting with an oil solvent having a specific gravity not higher than that of the meal. The use of solvent sprays and hot vapors are reported [31] to be effective in obtaining high oil yields, and a mixture of aromatic hydrocarbons with 1 to 10% of ethyl alcohol will effectively extract cottonseed oil and phosphatides to produce high-crude oil yields.[32]

Extracted cottonseed oil of light color has been obtained by hot extraction (78° C.) with 85% (by weight) ethyl alcohol.[33] Upon cooling, the miscella separates into two layers; the lower oil layer is reported to be much lighter in color and lower in free fatty acid content than benzine-extracted oil. The upper layer contains an alcoholic solution of oil, free fatty acids, and extraneous materials.

A somewhat similar process using furfural and other solvents has been

[24] H. Bollman, U.S. Pat. 1,653,201 (1927).
[25] A. L. Davis and L. H. Bartlet, U.S. Pat. 2,191,455 (1940).
[26] E. C. Koo and P. S. King, *Ind. Research China,* **5,** 137–141 (1936).
[27] H. Rosenthal, U.S. Pat. 2,254,245 (1941).
[28] E. C. Koo and S. M. Chang, *Ind. Research China,* **5,** 338–343 (1936).
[29] A. Chernukhin, *Masloboino Zhirovoe Delo,* **13,** No. 3, 7–8 (1937).
[30] R. O. Boykin (to N. Russel Vail), U.S. Pat. 1,721,686 (1929).
[31] S. Il'in, *Masloboino Zhirovoe Delo,* **14,** No. 3, 5–8 (1938).
[32] B. Rewald, U.S. Pat. 1,917,734 (1933).
[33] M. Sato, T. Inaba, and K. Kitagawa, *J. Soc. Chem. Ind. Japan,* **38,** 50 (1935).

patented [34] for separating glyceride oils by extracting them at a temperature not substantially below 104° F. The furane–oil solution is cooled to effect a separation into two liquid phases, one of which contains relatively unsaturated glycerides and the other, highly saturated glycerides.

Many equipment patents for extracting oil from cottonseed meats have been issued, some of which embody excellent ideas, as for example,[35] an inclined conveyor extractor with pressing worms at the end of each conveyor. Another uses the combination of solvent and pressure,[36] and still another utilizes vacuum filters with calcium hydroxide being used to prevent clogging.[37]

The above brief account describing some of the highlights of solvent extraction investigations as applied to cottonseed oil indicates that much effort has been spent on perfecting a usable process. To date (June, 1946) no commercial solvent extraction unit is in operation in the United States, although plant tests of various equipment, mostly of the batch type, have been made from time to time.

As is generally known, several continuous solvent extraction systems have been found very satisfactory and efficient for extracting the oil from soybeans. At present, about 30–35% of the United States' soybean processing capacity is of the solvent type. A large portion of the recently built soybean processing plants have employed solvent extraction, because by this method the processor is able to obtain about 55–65 pounds additional oil per ton of beans as compared with the next most efficient method. Processing costs, except for higher investment charges for solvent extraction, are of approximately the same order.

The above experience on soybean solvent extraction is mentioned to emphasize the fact that for cottonseed extraction the picture is somewhat different. Since cottonseed meal yields are only about 830–880 pounds per ton compared with about 1,550–1,600 pounds per ton for soybeans, one can see at a glance that the possible improvement in oil yield is considerably less. The estimated increased oil yields obtainable by extracting cottonseed meats are 33 to 40 pounds per ton, depending on the efficiency of the present hydraulic pressing operation. Compared with the more efficient expeller processing of cottonseed, the increased oil yield obtained by extraction is about 26 to 31 pounds per ton.

Soybeans contain about 18–20% oil and can be flaked rather easily with proper moisture control; furthermore, the structure of the flakes is maintained during the extraction process. Cottonseed meats contain about

[34] S. E. Freeman (to Pittsburgh Plate Glass Co.), U.S. Pats. 2,200,390 (1940) and 2,200,391 (1940).

[35] C. Drahn (to Firm Fried Krupp, Grusonwerk Aktien), U.S. Pat. 1,685.534 (1928).

[36] E. Lawrence, Jr., U.S. Pats. 1,748,356 (1930) and 2,154,339 (1939).

[37] R. O. Boykin (to N. Russel Vail), U.S. Pat. 1,775,154 (1930).

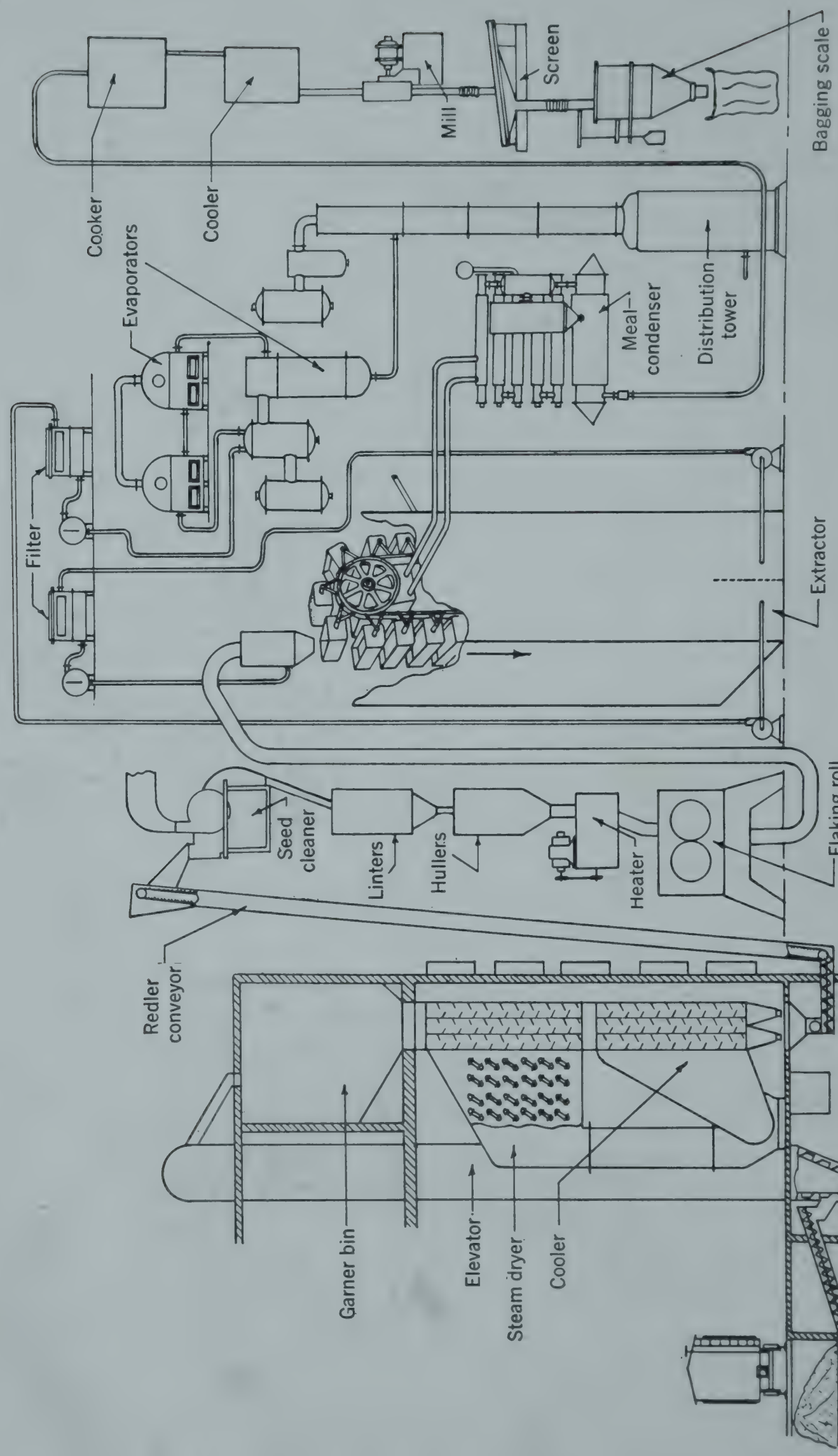


Fig. 169. Basket- or Bollman-type extractor.

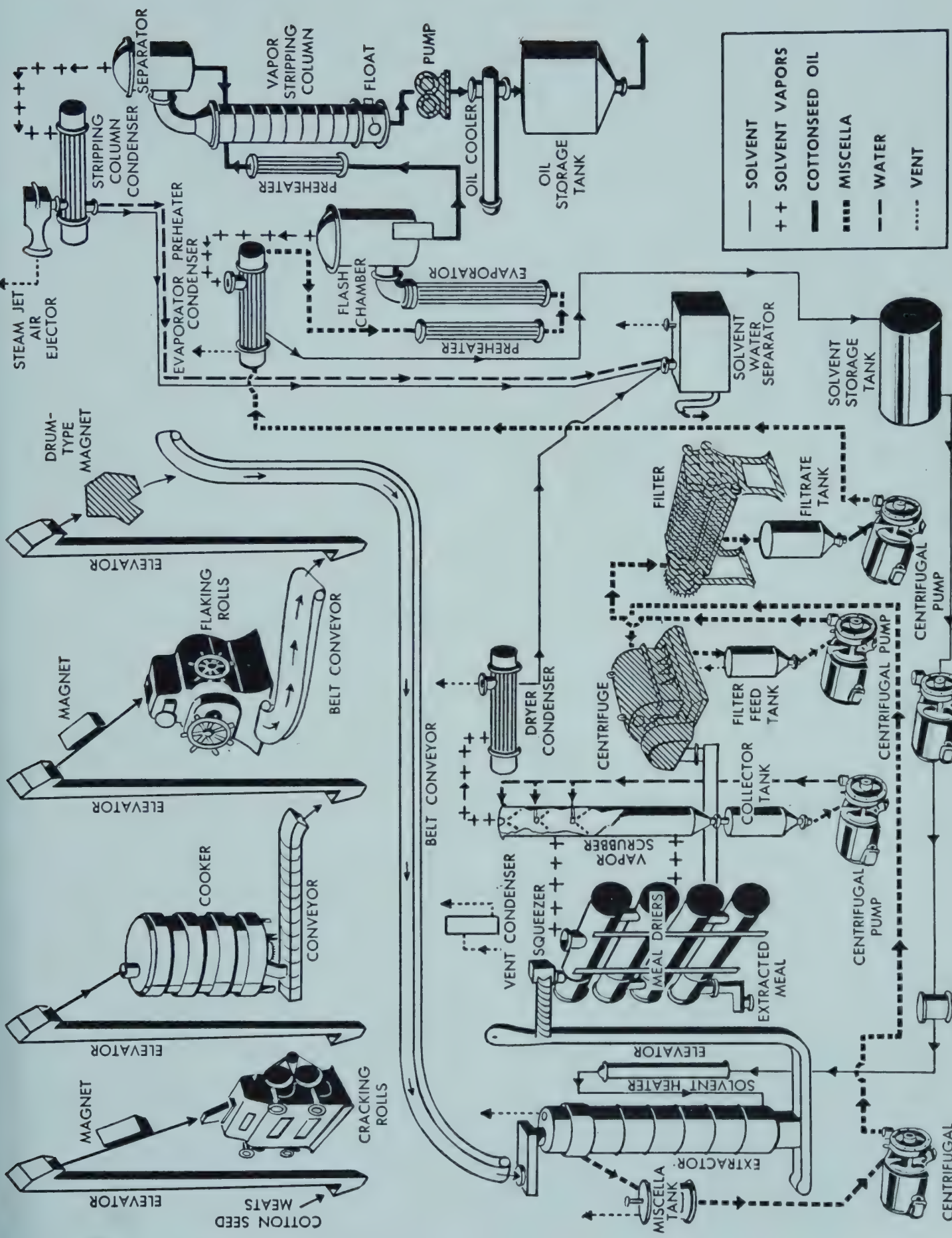


Fig. 170. Allis-Chalmers extraction system. (Courtesy *Allis-Chalmers Mfg. Co.*)

35% oil and can also be flaked readily, but the flake structure breaks down during the extraction process. Hence the equipment used successfully for extracting soybeans may offer some difficulty when used on cottonseed.

B. Types of Continuous Extractors

The types of extraction systems in successful use in the United States for extracting soybeans, and in Europe for extracting other oilseeds as well, are shown in Figures 169 to 173. Of these, the basket extractor (Bollman), the Allis-Chalmers, and the U-tube extractor (Hildebrandt) are in most common use in large installations. The Ford (Fig. 172) and the conveyor type (the latter using noninflammable trichlorethylene as a solvent) have been used successfully in smaller soybean extraction units.

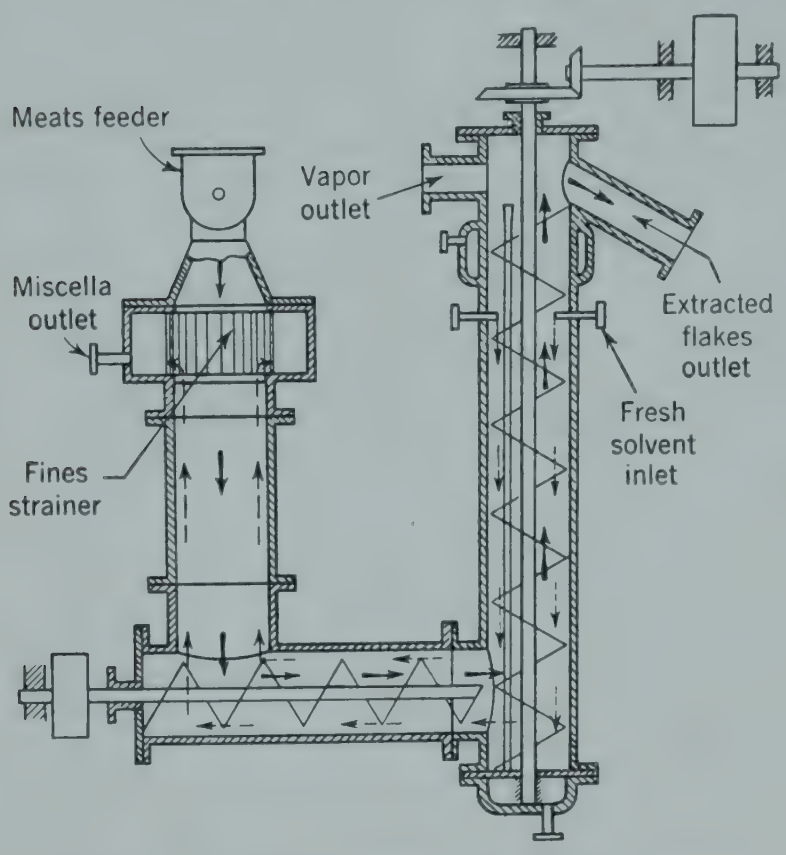


Fig. 171. Hildebrandt or U-tube extractor.

One advantage of the basket- or Bollman-type extractor (Fig. 169) is that miscella filtration is a relatively simple procedure, since each draining basket acts as a filter for the basket above it. The miscella is, therefore, quite clear and the subsequent filter requires attention only at very infrequent intervals. This is an important consideration in solvent processing.

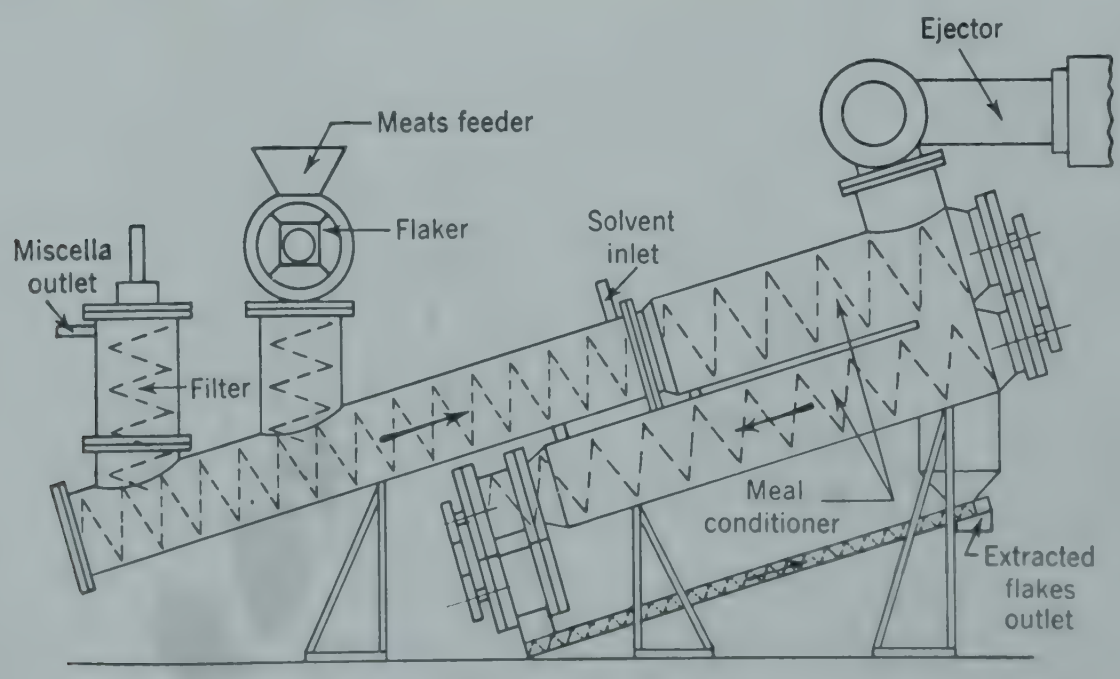


Fig. 172. Ford extractor.

The Allis-Chalmers (Fig. 170) and the U-tube or Hildebrandt (Fig. 171) extractors are undoubtedly simpler mechanical units. However, mis-

cella filtration is more of a problem with these, since the conveyor action tends to produce some "fines."

The Fauth-type extraction system (Fig. 173), using alternate mixers and enclosed solvent expellers, is reported to operate well on various oilseeds, particularly those high in oil content. The extraction principle using pressure is sound, although the mechanical maintenance of the equipment may be relatively difficult.

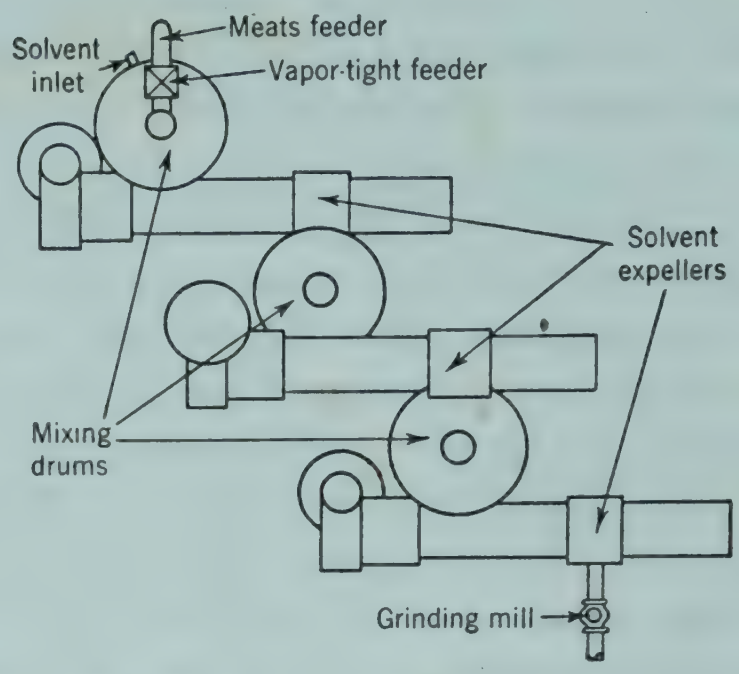


Fig. 173. Fauth or pressure-type extractor.

C. Mill Installations for Extraction of Cottonseed

Recently it has been reported [38] that large-scale solvent extraction units will be installed at several mills to be ready for operation in the 1946–47 crop season. One of these is a basket extractor and the others are Allis-Chalmers system extraction units.

Reference to Figures 169 and 170 will indicate the various steps in the extraction operation. A cottonseed dryer is shown in Figure 169. The seed dryer is necessary only when processing high-moisture seed. It may be used to dry the seed for storage or sent directly to the mill as indicated. Seed up to 14–15% in moisture content can be processed without a seed dryer, since the meats can be dried sufficiently by the "heater" before the flaking rolls to produce proper flaking. Seed of higher moisture content must be dried in a seed dryer or reduced in moisture content by air-cooling.

The processing steps through the huller room remain unchanged, except that it appears desirable to separate the hulls as much as possible to improve flaking. The "heater" ahead of the rolls is used to condition the flakes to obtain a desirable flake structure. The flakes are transported to the baskets where they are flooded with half miscella on the "down" side and fresh solvent on the "up" side. The extracted meats are dumped from the baskets at the top of the extractor and conveyed to the meal conditioners. The solvent retained in the extracted flakes is recovered in the meal conditioners, after which the flakes may be toasted, if desired, cooled, and ground to meal.

The full miscella, containing about 20–25% oil as it comes from the bottom of the left side of the extractor (Fig. 169), is filtered and thereafter passes through a series of evaporators and stills to remove all traces of solvent from the oil.

[38] See the *Cotton and Cotton Oil Press*, **46,** No. 5, A-4 (1945).

The general extraction processing through the Allis-Chalmers unit is very similar as can be seen by following the flow of material in Figure 170.

Some of the above processing operations may be altered to meet certain requirements. For example, in order to detoxify the gossypol in cottonseed meats, a suggestion has been made,[39] based on laboratory work, to roll and cook the meats as performed at present in the hydraulic process and then extract the cooked meats. The resulting meal would be like hydraulic meal in quality.

Harris [40] and others have suggested extraction of the gossypol by a two-step extraction process in which the material would be extracted with a hydrocarbon, like hexane, and then with a solvent, like ethyl ether, benzene, or a chlorinated hydrocarbon. Also, the oil, gossypol, and coloring matter can be extracted simultaneously with a solvent, such as ethyl ether, a chlorinated hydrocarbon, or a mixture of a chlorinated hydrocarbon and aliphatic hydrocarbons, and other solvents. Washing the miscella with dilute caustic or soda ash solutions is reported to remove the gossypol and coloring matter.

The resulting meal, when the gossypol is extracted, is nontoxic and the quality of the proteins is optimum for feeding, since the latter have not been denatured by heating at a high temperature. Successful laboratory refining and bleaching of the oils in the miscella have been reported.[40, 41]

The introduction of solvent extraction methods to cottonseed processing will open new fields for development of industrial products from the undenatured protein.[42] The entire solvent extraction development for cottonseed, which appears to be getting underway, will be watched with keen interest by all those interested in cottonseed products.

[39] H. S. Olcott, *Ind. Eng. Chem.*, **33,** 611–615 (1941).
[40] W. D. Harris, *Oil Mill Gazetteer,* **50,** No. 5, 14–21 (1945).
[41] B. H. Thurman (to Refining, Inc.), U.S. Pat. 2,260,731 (1941).
[42] R. Nickerson (to Cotton Research Foundation), U.S. Pat. 2,194,835 (1940).

CHAPTER XVI

ECONOMICS OF COTTONSEED CRUSHING

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Memphis, Tennessee

I. General Characteristics of the Industry

A. NUMBER AND LOCATION OF MILLS

The cottonseed crushing industry of the United States comprises, at the present time (1945), 382 operating mills.[1] In addition, there are about 40 other mills equipped to crush cottonseed that are not operating on that crop at present. Some of this latter group are engaged in crushing other oilseeds; most of them are simply inoperative and may eventually be dismantled, or they may resume operations when and if local conditions warrant. The location of the presently active mills, together with the production of cottonseed, by states, is shown in Table 171. To indicate trends, comparative data for the 1924–25 and 1934–35 seasons [2] are included in the table.

B. TRENDS IN SIZE AND DISTRIBUTION OF MILLS

The total number of cottonseed crushing mills has been reduced significantly during the past twenty years. The greater part (80%) of this decline has taken place in four states: North and South Carolina, Oklahoma, and Texas. Two factors have been largely responsible. First has been the decrease in cottonseed production in certain areas. This has been notable in Oklahoma and Texas, and has occurred on a somewhat smaller scale in North Carolina and Georgia. The second factor stems from the historical pattern of the development of the industry. As was pointed out in a previous chapter, the cottonseed crushing industry came into being during a period when transportation facilities in the southern States were very limited. Since seed could not readily be moved to centrally located mills, the mills tended to locate near the seed. Mill operation in the early

[1] U.S. Bureau of the Census, *Cotton Production and Distribution, Season of 1944–45,* Bulletin 182.

[2] In the cottonseed crushing industry, the "season" or "year" corresponds to the crop year, Aug. 1 to July 31.

TABLE 171

Number of Operating Cottonseed Crushing Mills and Production of Cottonseed, by States, 1944–45, 1934–35, and 1924–25[a]

State	1944–45		1934–35		1924–25	
	Number of mills	Seed produced 1000 tons	Number of mills	Seed produced 1000 tons	Number of mills	Seed produced 1000 tons
Ala.-Fla.	29	386	33	423	32	437
Arizona	4	56	[b]	[b]	[b]	[b]
Arkansas	25	558	29	389	30	488
California	7	128	7	115	[b]	35
Georgia	42	320	54	431	51	445
Louisiana	18	250	18	215	19	219
Mississippi	41	795	42	508	43	487
North Carolina	32	286	44	280	53	366
Oklahoma	23	259	34	141	44	671
South Carolina	25	356	32	303	47	357
Tennessee	14	210	16	180	17	158
Texas	115	1068	158	1072	171	2201
All other states	7	229	11	226	23	187
Total	382	4901	478	4282	530	6051

[a] From U.S. Bureau of the Census, *Cotton Production and Distribution*, Bulletins 158, 172, and 182.

[b] Included in "All other states."

days of the industry is reported to have been quite profitable.[3] Machinery manufacturers promoted the erection of many mills as a means of selling their equipment. This combination of factors resulted in a large number of relatively small units close to the source of raw material. In the early part of the present century, the number of mills exceeded 900.

As transportation and marketing facilities developed, each mill was able to extend the area in which it could purchase seed. Competition increased and those mills that were uneconomically located or designed or had relatively inefficient management went out of business. There has been a steady downward trend in the number of mills for more than thirty years.

This trend toward fewer and larger units is illustrated in Table 172, showing the number and percentage of mills according to the volume of seed crushed for the latest complete season and for ten and twenty years previous. To show the change over the past twenty years, the number of mills in each (volume) class in 1944–45 has been expressed as a percentage of the number in the same class in 1924–25. It will be noted that the only increase has occurred in that group of mills crushing 20,000 tons or more seed per year. All other groups have declined and the smaller the volume of seed crushed the greater has been the rate of decline. For convenience,

[3] G. W. Covington *Cotton Oil Press*, **5**, No. 2, 89–90 (1921).

all mills [4] crushing less than 5,000 tons of seed annually may be classed as "small," those crushing 5,000 but less than 20,000 tons as "medium," and those crushing more than 20,000 tons as "large." Under this classifica-

TABLE 172

Number and Per Cent of Cottonseed Crushing Mills, by Volume of Seed Crushed, 1944–45, 1934–35, and 1924–25[a]

Seed crushed, tons	1944–45		1944–45 as per cent of 1924–25	1934–35		1924–25	
	Number of mills	Per cent		Number of mills	Per cent	Number of mills	Per cent
Under 1,000	8	2.1	44.4	43	9.0	18	3.4
1,000–1,999	21	5.5	48.8	42	8.8	43	8.1
2,000–4,999	81	21.2	56.6	138	28.9	143	27.0
5,000–9,999	111	29.0	72.5	141	29.5	153	28.9
10,000–19,999	108	28.3	76.6	82	17.1	141	26.6
20,000 and over	53	13.9	165.6	32	6.7	32	6.0
Total	382	100.0	72.1	478	100.0	530	100.0

[a] From U.S. Bureau of the Census, *Cotton Production and Distribution*, Bulletins 158, 172, and 182.

TABLE 173

Number and Daily Capacity of Cottonseed Crushing Mills, by Size of Community, 1944–45[a]

Population of community	Mills				Capacity per 24-hour day			
	Actual		Cumulative		Actual		Cumulative	
	Number	Per cent	Number	Per cent	Tons	Per cent	Tons	Per cent
Under 5,000	151	39.5	151	39.5	11,472	31.7	11,472	31.7
5,000–9,999	79	20.7	230	60.2	6,761	18.7	18,233	50.4
10,000–24,999	65	17.0	295	77.2	6,450	17.8	24,683	68.2
25,000–49,999	23	6.0	318	83.2	2,395	6.6	27,078	74.8
50,000–99,999	35	9.2	353	92.4	4,698	13.0	31,776	87.8
100,000 and over	29	7.6	382	100.0	4,439	12.2	36,215	100.0

[a] Data compiled as follows: number of mills and capacity from *The International Green Book, 1944–45*, Cotton and Cotton Oil Press, Dallas, 1944, and confidential information furnished the author by mills; population of communities from 16th Census of the U.S. 1940, *Population*, Vol. 1.

tion, the number of small mills has decreased 46.1% since 1924–25. During the same period, the number of medium-sized mills has been reduced by 25.5%, while the large mills have increased 65.6% in number.

[4] This classification is purely arbitrary. In some localities, for example, a mill that crushes 10,000–12,000 tons annually may properly be considered a small mill. In other areas, it may be considered a large mill.

In interpreting Table 172, the shift of particular mills from one class to another should be recognized. The 21 mills that crushed 1,000–1,999 tons in 1944–45, for example, were not necessarily in the same class twenty years previous. At that earlier date, some of them may have crushed over 2,000 tons and some less than 1,000 tons. Likewise, the 32 mills that crushed more than 20,000 tons in 1924–25 are not all in that class today. Some are crushing less and others have gone out of business. There has been a continuous shift between the various classes.

The trend toward centrally located units, illustrated in Table 172, has not proceeded to an extent comparable to that of a number of other agricultural processing industries. Cottonseed crushing is still largely a "small town" industry. Table 173 presents a tabulation of the number of mills and of estimated daily crushing capacity by size of community. Approximately 40% of the mills are located in communities of less than 5,000 population. Another 20% of the industry's plants are located in towns of 5,000 to 10,000 population. In other words, 60% of the operating units are located in what may be appropriately termed small towns. Only 7.5% of the mills are in the large cities of 100,000 or more population.

C. Difficulties in Transportation of Cottonseed

The fact that all cottonseed crushing mills are located in the cotton-producing states (see Table 171) and are generally distributed throughout those states is a result of the physical character of cottonseed. Compared with other agricultural commodities, cottonseed are of very low density. A bushel of seed weighs approximately 32 pounds, compared with 56 pounds per bushel for corn and flaxseed, and 60 pounds per bushel for wheat and soybeans.[5] The average railway freight car carries 28.9 tons of cottonseed, compared with 45.9 tons of flaxseed, 48.2 tons of corn, or 50.0 tons of wheat.[6] This bulkiness of cottonseed makes it uneconomic to transport seed for crushing purposes more than 200–300 miles as a maximum. Actually, the major proportion of the seed crushed moves less than 100 miles. According to a report of the Interstate Commerce Commission, the average rail haul of cottonseed has been about 75 miles.[7] Truck hauls undoubtedly average less. One study, confined to Louisiana, reports the average shipping distance for seed in that state (by both rail and truck) as 46.5 miles.[8] While the average shipping distance in Louisiana is less than that of some other areas, the national average may be estimated at between 50 and 75 miles.

[5] U.S. Dept. Agr., *Agricultural Statistics,* 1944, p. 6.
[6] U.S. Dept. Agr., *Agricultural Statistics,* 1944, p. 566.
[7] *188 Interstate Commerce Commission 605,* p. 615.
[8] J. F. Hudson, "Marketing of Cottonseed by Farmers and Ginners in Louisiana," *Master's Thesis,* Louisiana State Univ., 1945.

D. Mill Capacity

Referring to Table 173, it will be noted that the distribution of crushing capacity varies somewhat from that of the number of mills. About 50% of the industry's capacity (compared with 60% of the mills) is located in communities of less than 10,000 population. In each population group above 10,000 the percentage of capacity exceeds that of the number of mills. In other words, there is a tendency for capacity per mill to vary directly with the size of the community. Transportation facilities are one of the major factors responsible for this tendency.

Total daily capacity of the industry, as estimated in Table 173, is 36,235 tons. Assuming 300 days as a "normal" year's operation to allow for repairs, holidays, etc., the industry could crush 10,870,500 tons of seed annually. This is considerably in excess of the quantity of seed available for crushing. In recent years, the industry has operated at only 40–45% of potential annual capacity. This relationship of potential capacity to available raw material has had an important influence upon the industry's operations and will be discussed in more detail at a later point.

E. Ownership of Mills

Ownership in the cottonseed crushing industry is about equally divided between companies operating a single mill and those operating more than one plant. The latter are commonly referred to as "group" mills. Of the 382 active mills in the 1944–45 season, 189 were single enterprises and 193 were group mills.[9] While there is a general tendency for the group mills to be larger than the singly owned units, there is no uniformity of such a relationship. The largest firm in the industry, in point of number of mills operated, has a substantial number of small units—smaller in fact than many of the single enterprise mills. Size of the individual mill depends more upon location and management policies than upon single or multiple ownership.

Ownership of the mills may be further classified on the basis of whether or not the owner refines and further processes cottonseed oil into finished products.[10] The manufacturers of shortening and other finished cottonseed oil products entered the crushing industry many years ago to assure themselves at least a part of their oil requirements. They not only take the oil produced by their own mills, but also purchase oil from the other mills. In 1944–45, 122 mills were operated by finished oil products manufacturers; 260 mills were not so affiliated. Each finished product manufacturer engaged in the crushing industry operates more than one mill.

[9] Compiled from *The International Green Book, 1944–45,* Cotton and Cotton Oil Press, Dallas.

[10] There are several individual and group mills that put cottonseed oil through the first refining process. Such mills, however, do not produce finished products and are not included in the group referred to here.

During recent years, there has been no well-defined trend or shift in the ownership of crushing mills. Since 1939–40, there has been a net decrease of 64 operating mills. Thirty-seven of these were single-enterprise mills; 27 were owned by companies having more than one plant.[11] While the mortality rate has been higher among single-enterprise mills, the difference has not been great. Actually, the number of group mills that have failed during the past five years is greater than the net decline of the 27 shown above. This is explained by the fact that several of the multiple-unit firms have moved mills from locations that have proven unprofitable to points where profitable operations appear possible. While such action is theoretically possible for the single-enterprise mill, the latter appears to be much less mobile. Lack of capital resources and of information as to promising locations are probably the principal reasons for such immobility. The single-enterprise mill tends to be tied to the community in which it originally locates and it usually succeeds in that location or it goes out of existence.

II. By-Products and Joint Products

Unlike the majority of agricultural commodities, whose production responds generally to market demand, cottonseed production is completely dependent upon the production of another commodity—lint cotton—which has wholly different uses and is subject to an entirely different set of market conditions. In the physical sense, cotton is a joint crop, its components being lint and seed. In terms of monetary income yielded the producer, lint is considerably the more valuable of the two components. Over the past decade, it has accounted for 82.0% of the total value of the cotton crop, compared with 18.0% derived from seed.[12] Economically, therefore, seed are a by-product, the production of which is determined primarily by the production of cotton lint.

A. Ratio of Seed to Lint

So closely is the production of seed dependent upon the production of lint that the Census Bureau, in estimating cottonseed production, has until recently employed the constant ratio of 65 pounds of seed to 35 pounds of lint. On this basis, each 500-pound (gross weight) bale of lint cotton would be accompanied by the production of 888 pounds of cottonseed. Actually, this ratio varies from year to year, from area to area, with the variety of seed planted, and with soil and climatic conditions. Beginning with the 1943–44 season, the Census Bureau modified its lint–seed ratio to conform approximately to actually realized yields. The latter now

[11] Compiled from *The International Green Book, 1939–40* and *1944–45*, Cotton and Cotton Oil Press, Dallas.

[12] Computed from U.S. Bureau of the Census, *Cotton Production and Distribution*, Bulletins 173–182.

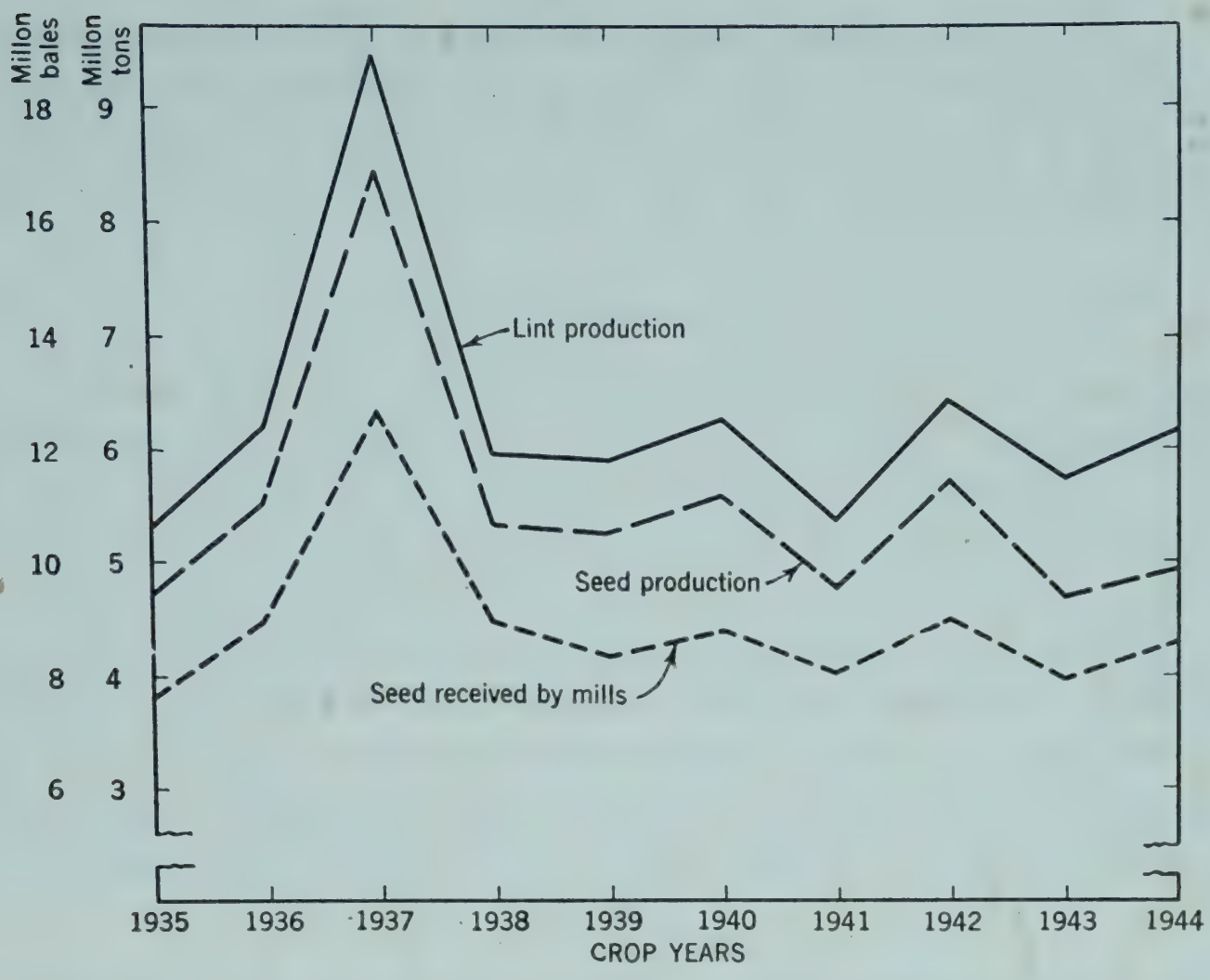


Fig. 174. Cotton lint production, cottonseed production, and volume of seed received by crushing mills, crop years 1935–1944.

average about 63 pounds of seed to 37 pounds of lint from the United States as a whole. The relationship between lint production, seed production, and the quantity of seed sold to the mills is shown in Figure 174.

B. Proportion of Total Seed Crushed

The proportion of cottonseed production that is sold to the crushing mills each year is reasonably constant. During the past decade, it has ranged from 77.4 to 89.0%, averaging 80.7%.[13] The percentage of seed marketed is influenced by a number of factors, some of which are compensating. Out of each year's crop, a minimum quantity of seed must be retained for the following year's planting. The smaller the current crop, the larger will be the percentage required for this purpose. If this was the only factor present, we could expect the percentage of seed sold for crushing to vary directly with the size of the crop. Actually, this factor is more than offset by the influence of price. A small crop of cottonseed usually brings a higher price per ton than a large crop, and the incentive to sell is consequently greater. Also, in years of large crops, seed sellers carry over some seed in the hope of realizing a higher price the following season. As a result, there is a definite tendency for the percentage of cottonseed

[13] Actually, the range is probably smaller than shown. The Census Bureau's use of the 65/35 seed/lint ratio prior to 1943–44 tended to maximize seed production and minimize the percentage crushed.

production sold for crushing in any one year to vary inversely with the size of the crop. Thus the price, while not a factor in determining the volume of seed production, does exert an influence upon the quantity sold to the crushing mills. Size of the crop, however, is the principal determining factor.

C. Yields of the Four Joint Products

From cottonseed, the crushing mills produce four joint products: oil, cake or meal, hulls, and linters.[14] The average yields of these four products per ton of seed crushed, for the past ten seasons, are shown in Table 174. The total yield of products per ton is relatively constant with a variation of less than 2.0% between high and low yields during the decade. Oil and meal yields are also quite stable, showing a variation of 6.9 and 6.2%, respectively, during the same period.[15] The yield of hulls is more variable with a difference of 12.1% between high and low. Linters yields show the greatest variation—32.9% during the ten-year period.

The yields shown in Table 174 are a function of both the economy and

TABLE 174

Average Quantity and Percentage of Cottonseed Products Produced per Ton of Seed Crushed, 1935–36 through 1944–45[a]

Season	Oil		Cake or meal		Hulls		Linters		Total[b]	
	Pounds	Per cent	Pounds	Per cent	Pounds	Per cent	Pounds	Per cent	Pounds	Per cent
1935–36	305	15.3	911	45.5	518	25.9	143	7.2	1877	93.9
1936–37	303	15.2	903	45.1	509	25.4	156	7.8	1871	93.5
1937–38	310	15.5	895	44.7	514	25.7	144	7.2	1863	93.1
1938–39	315	15.8	905	45.2	519	25.9	154	7.7	1893	94.6
1939–40	319	15.0	907	45.3	508	25.4	160	8.0	1894	94.7
1940–41	324	16.2	888	44.4	504	25.2	171	8.6	1887	94.4
1941–42	312	15.6	874	43.7	495	24.7	186	9.3	1867	93.3
1942–43	311	15.6	887	44.3	482	24.1	190	9.5	1870	93.5
1943–44	313	15.7	928	46.4	469	23.4	185	9.3	1895	94.8
1944–45	311	15.6	919	45.9	463	23.1	182	9.1	1875	93.7
Average	312	15.6	901	45.1	499	25.0	166	8.3	1878	94.0

[a] From U.S. Bureau of the Census, *Cotton Production and Distribution*, annual editions for years shown. Percentages computed by author.

[b] The difference between figures in this column and 2,000 pounds and 100% is accounted for by manufacturing loss, primarily in the form of moisture.

[14] The distinction between "lint" and "linters" should perhaps be noted. "Lint" refers to the fibers generally known as cotton which are removed from the seed by ginning. "Linters" are the short fibers that are not removed in ginning but adhere to the seed as they reach the crushing mill.

[15] It should be kept in mind that reference is being made to *average* yields. The yield of products per ton varies widely with individual lots of seed. For example, see G. S. Meloy, *Variations in the Composition and Grade of Cottonseed Produced in the States of Alabama, Georgia, North Carolina and South Carolina, Crop Years 1934–35 to 1937–38*, U.S. Dept. Agr., Washington, 1939.

technology of the industry. Original efforts to crush cottonseed had as their prime objective the recovery of oil, which at that time was the only product with a generally recognized commercial value. To prevent too great an absorption and consequent loss of oil, it was necessary to remove the hulls. Since any considerable quantity of linters on the hulls makes separation from the meats difficult and also causes a loss of oil, it was later found that the removal of linters as a first step was essential to efficient mill operation. The development of markets over the years has given value to the products other than oil. Despite this, however, the greater economic value of the latter establishes maximum oil recovery as the primary present day objective of crushing operations.

The value of cottonseed products per ton of seed crushed, in dollars and as a percentage of the total, is shown in Table 175. The importance

TABLE 175

Average Value of Cottonseed Products per Ton of Seed and Percentage of Total Value Represented by Each Product, 1935–36 through 1944–45[a]

Season	Oil		Cake or meal		Hulls		Linters		Total, dollars
	Dollars	Per cent	Dollars	Per cent	Dollars	Per cent	Dollars	Per cent	
1935–36	26.57	60.5	10.15	23.1	1.72	3.9	5.49	12.5	43.93
1936–37	27.38	53.8	14.62	28.6	2.33	4.6	6.61	13.0	50.94
1937–38	19.20	57.3	9.93	29.6	1.42	4.2	2.99	8.9	33.54
1938–39	19.37	56.5	10.56	30.8	1.59	4.7	2.74	8.0	34.26
1939–40	18.68	48.7	13.01	33.9	2.10	5.5	4.56	11.9	38.35
1940–41	17.62	46.6	11.96	31.6	1.99	5.3	6.23	16.5	37.80
1941–42	37.86	58.2	16.86	25.9	1.97	3.0	8.36	12.9	65.05
1942–43	39.54	59.7	16.23	24.5	2.10	3.2	8.36	12.6	66.23
1943–44	39.83	54.3	22.45	30.6	3.00	4.1	8.02	11.0	73.30
1944–45	39.19	54.0	22.31	30.7	3.06	4.2	8.03	11.1	72.59
Average	27.98	55.2	14.54	28.7	2.09	4.1	6.06	12.0	50.67

[a] Computed from U.S. Bureau of the Census, *Cotton Production and Distribution*, annual editions for years shown.

of oil, as compared with the other products, is readily apparent. Over the ten-year period, it accounted for only 15.0% of the yield in terms of volume, but it represented 55.2% of the total value. Cake or meal, representing 28.7% of the value, was second in importance, with linters and hulls accounting for 12.0 and 4.1%, respectively. On the basis of these relative values, it is obviously to the mill's financial advantage to obtain the maximum yield of oil per ton of seed processed. In so doing, the mill must produce a certain quantity of cake or meal. This fact explains the relatively small variation in the yields of oil and cake or meal noted in Table 174. Such variation is principally the result of climatic conditions.

The case of hulls and linters is somewhat different. As noted previously,

the production of these products is essential to the maximum recovery of oil. Variation in output per ton is possible, however, within certain limits. The removal of linters from seed is one of the most expensive operations performed by the crushing mill. When the market price of linters is low, the tendency is to remove only the quantity necessary for efficient milling. When the price is high, there is a tendency for the cut per ton to be increased. During recent years, there has been a significant increase in the yield of linters per ton of seed crushed. This has been partly a response to favorable prices and partly the result of governmental directives to produce the maximum possible quantity for war purposes.

As would be expected, there is an inverse relationship between the per-ton yield of linters and hulls. As the quantity of linters removed from the seed is increased, the yield of hulls tends to decline. This relationship is not perfect. Climatic factors affect the relative yield of these two products, as they do the yield of oil and meal. Also, in periods of strong demand for cake or meal, the available supply of this product may be slightly extended by permitting more hulls to enter into it. This has occurred during the war years.

D. Allocation of Crushing Costs

The cottonseed crushing mill makes no attempt to allocate costs among the individual products. Such an allocation would be quite meaningless. The mill seeks to obtain the maximum per ton product income relative to operating costs. It can vary the per-ton yield of products slightly in response to market demand, but the total output of products is dependent primarily upon the volume of cottonseed reaching the mills which, in turn, depends upon cotton production.

III. Seasonality of the Industry

A. Distribution—by Months—of Picking, Ginning, and Crushing Operations

Like most of the agricultural processing industries, cottonseed crushing is highly seasonal in nature. Cotton picking begins in south Texas in the early part of July and moves northward as the season advances. In the northern part of the Cotton Belt, picking usually begins about the middle of September. Variation of as much as two or three weeks, either earlier or later, may occur from year to year as a result of differences in the weather during the planting and growing seasons.

Once cotton has opened, it is picked rapidly. Here again, weather is the controlling factor. To avoid lowering the quality of both lint and seed, with consequent financial loss, it is necessary that cotton be picked before wet weather sets in, usually by the first of December. There are no actual

data on the rate at which cotton is picked, but since practically all cotton is ginned immediately after picking, the rate of picking and that of ginning may be considered synonymous. During the ten crop years 1935–1944, 92.0% of the crop was ginned prior to December 1—and 83.0%, during the three months of September, October, and November.[16] Since picking and ginning shift northward with the season, the rate at which the crop moves in particular localities is even more rapid than indicated by the above percentages.

Most of the cottonseed crop is sold by the farmer to the ginner at the time of ginning. Ginners generally do not have facilities to store and adequately preserve large quantities of cottonseed. This is particularly the case when seed are high in moisture. As a result, cottonseed move to the crushing mills at a rate only slightly less rapid than that of ginning. During the 1935–1944 period, 75.6% of the seed reached the mills prior

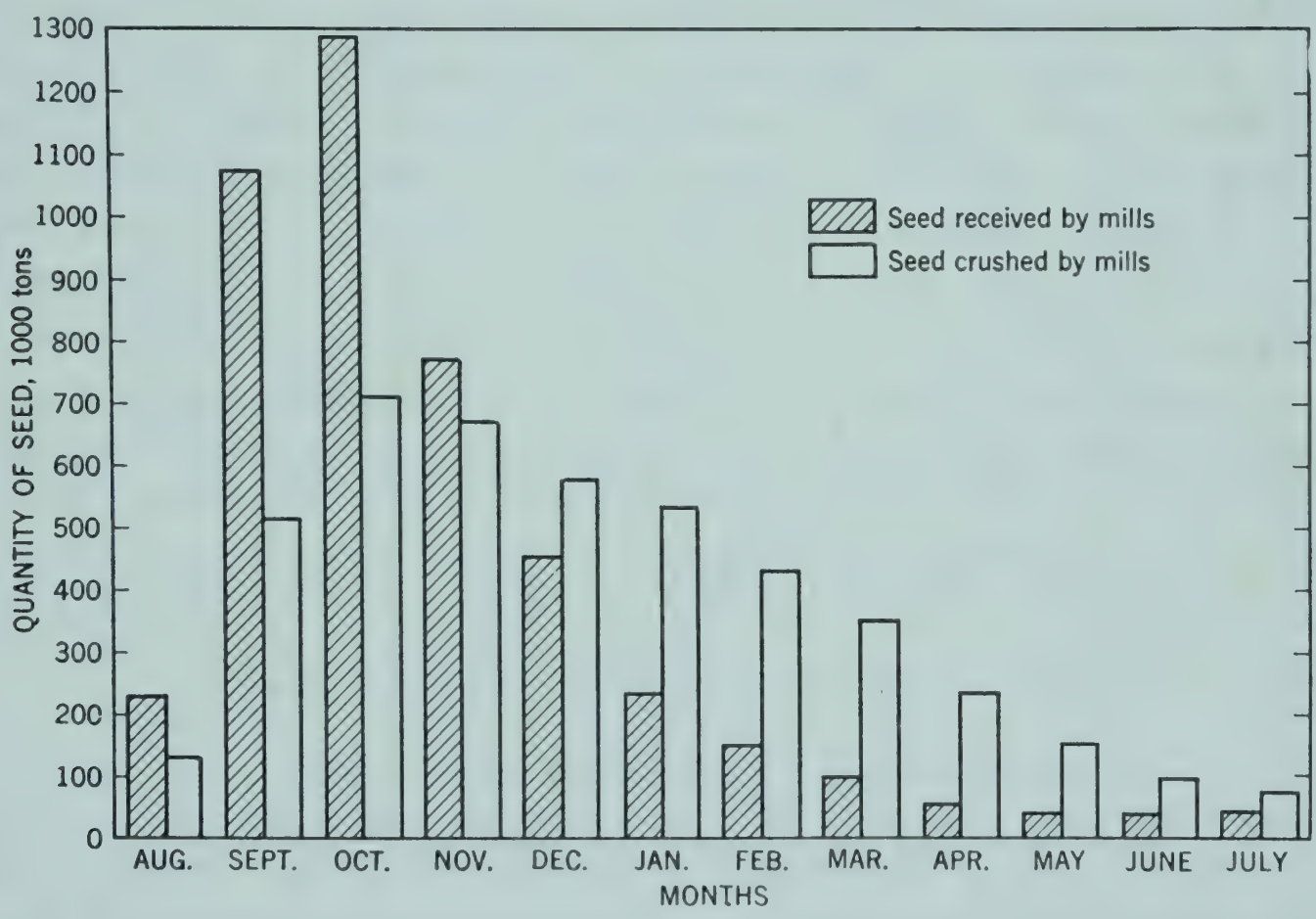


Fig. 175. Quantities of cottonseed received and crushed by mills, monthly average, seasons 1935–1944.

to December 1—and 70.4%, in the three-month period between September 1 and December 1. By the first of January, an average of 85.6% of all seed marketed for crushing purposes reached the mills.[17]

This heavy concentration of seed movement within a few months of the year has had an important influence upon the character and practices of the crushing industry. Taken in conjunction with the fact that cottonseed are perishable—sometimes highly so—it is responsible for the around-

[16] Computed from U.S. Bureau of the Census, *Cotton Production and Distribution.*
[17] From data supplied by U.S. Bureau of the Census.

the-clock operation that is traditional in the industry. During the crushing season, practically all mills operate on a 24-hour day. Like cottonseed marketing, but to a lesser degree, crushing is concentrated into a few months of the year. During the 1935–1944 period, 42.5% of the seed crushed was processed during the months of September, October, and November. By January 1, on the average, 58.5% of the seed has been crushed and by March 1, this figure rises to 80.0%. The quantities of seed received and crushed by the mills, by months, are illustrated in Figure 175.

The foregoing percentages and the data in Figure 175 tend to minimize the degree of seasonality in crushing operations. This results from the fact that the seasonal shift in picking and ginning, previously referred to, also occurs in cottonseed crushing, and from the further fact that a few mills, crushing a considerable volume of seed, operate most of the year. A more accurate indication of the degree of seasonality in the industry may be found in studies of the length of the operating season. On the basis of installed capacity and the quantity of seed available for crushing during the 1936–40 period, Meloy [18] has estimated that the industry could crush the entire crop in 125 days. Another study [19] of 197 identical mills shows that the average number of 24-hour days operated per press was 162 in 1937–38, 123 in 1938–39, and 113 in 1939–40. More recent data on this subject are, unfortunately, not available but it is doubtful that there has been any significant change in the length of the operating season since the foregoing studies were made. Some variation naturally occurs from year to year with changes in the size of the crop and, during World War II, there has been a tendency for the length of the operating season to increase due to the scarcity of labor and the low efficiency of the labor that was available. Generally, however, the change has not been great.

B. Problems Related to Seasonality

1. Fluctuation of Labor Requirements

The short operating season means that a large percentage of the industry's personnel is not employed (in oil milling) during a considerable part of the year. The wide seasonal fluctuation in employment in the cottonseed crushing industry is illustrated in the chart comprising Figure 176. This chart is based upon data for the calendar year 1939, the last year in which the Census of Manufactures was taken. The months of the year have been transposed to conform to the crop year. It will be noted that, from a low point in July, the number of workers employed increases about 25.0% in August, more than doubles in September, rises

[18] G. S. Meloy, *Proc. 46th Annual Convention, National Cottonseed Products Association*, May, 1942.

[19] National Cotton-eed Products Association, *Employment, Wages and Hours in the Cottonseed Crushing Industry, 1937–38, 1938–39, and 1939–40.*

another 10.0% in October, and then declines steadily through the balance of the crop year. Practically all mills maintain a minimum staff during the nonoperating season.

It is not to be inferred that workers in the cottonseed crushing mills are unemployed when the mills are not operating. A large percentage of mill labor has traditionally been drawn from agriculture. When the crushing season ends, such workers return to the farm. Other workers are drawn from industries and trades having employment peaks complementary to

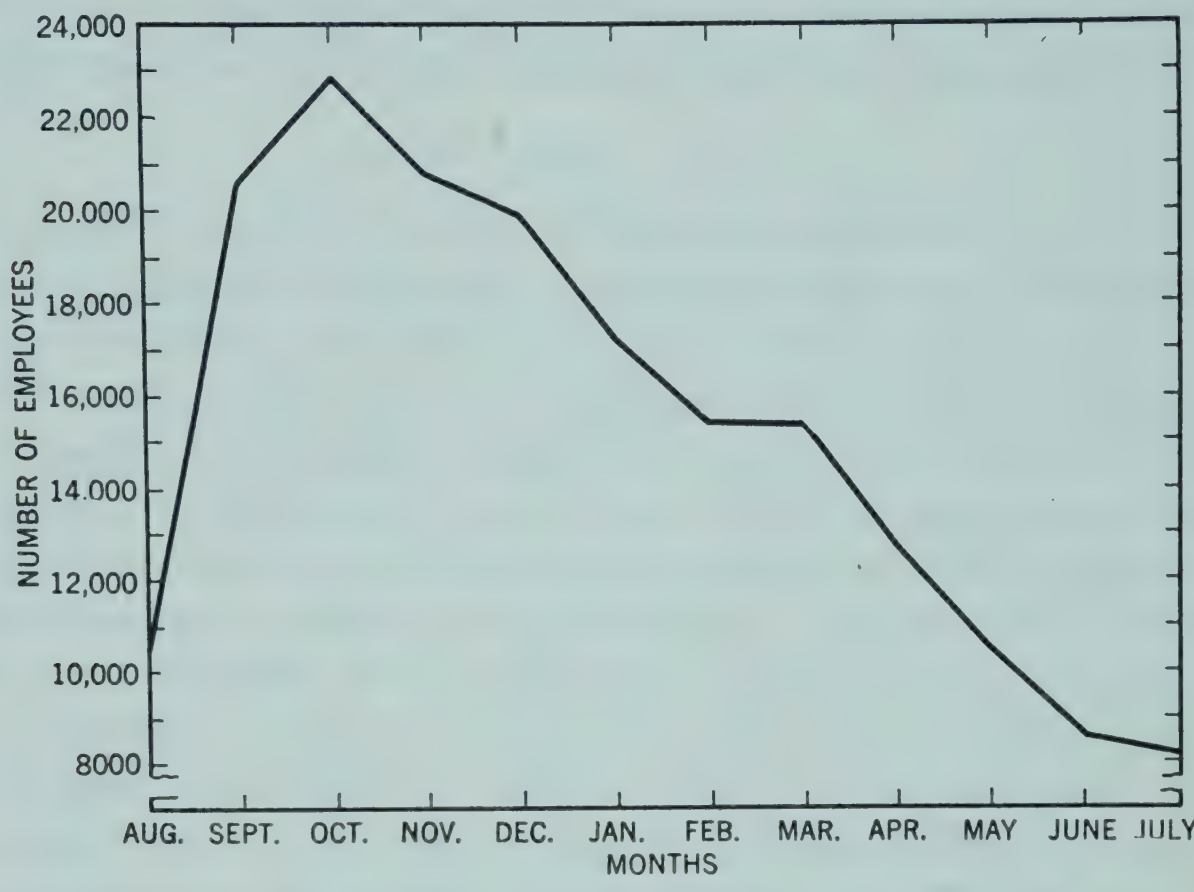


Fig. 176. Number of employees in cottonseed crushing, by months, calendar year 1939.

that of cottonseed crushing. A few mills have informal arrangements with such other businesses for the interchange of employees. In an effort to maintain more stable employment, many mills engage in enterprises other than crushing. The manufacture of fertilizer, mixed feeds and ice, and the distribution of agricultural supplies are among the activities most commonly associated with cottonseed crushing. Such activities are seasonal in nature and their fluctuations are generally complementary to crushing operations.

Despite such complementary enterprises and some effort to interchange employees with other industries, the rate of labor turnover in the crushing mills from one season to another is very high. Most mills retain a few key employees throughout the year but the bulk of oil mill labor is released at the close of the crushing season. Each year a considerable number of new employees are hired. While the majority of oil mill jobs are in the unskilled classification, the turnover of employees from year to year makes for relatively low labor efficiency. A somewhat crude measure of labor pro-

ductivity may be found in the "Value Added by Manufacture" as reported by the Census of Manufactures. On a per wage earner basis in 1939, this amounted to $2,153 in the cottonseed crushing industry compared with $2,312 for all manufacturing in the ten principal cotton-producing states and $3,300 in all other states.[20] Admittedly, the value added by manufacture is influenced by the nature of the industry involved. This value is usually lower, for example, in the first processing industries than in industries producing highly finished commodities. Even after allowance is made for this factor, however, the value added per wage earner in cottonseed crushing is below average, indicating relatively low labor efficiency.

2. Fixed Capital Charges

In addition to retarding the most effective utilization of labor, the short operating season results in idleness of the industry's capital equipment during a substantial portion of the year. With the exception of the power plant, oil mill equipment is not adaptable to operations other than crushing. When not in operation, such capital equipment is nonproductive. There is sound reason to believe that this fact has influenced the technology of the industry. Most cottonseed crushing mills are operated with hydraulic equipment. Other methods of oil extraction, claimed to be more efficient,[21] have been developed but their adoption by the industry has been very slow. Such methods require less labor than hydraulic equipment but they cost more to install. Since the cost of labor can be largely eliminated when a mill is not in operation while the cost of fixed capital continues throughout the year, equipment requiring the smallest investment possesses a considerable advantage. This relationship between the cost of labor and capital equipment has been especially applicable to cottonseed crushing because, until recent years, labor in the areas where the industry operates has been plentiful and inexpensive. With the sharp rise in wage rates that has occurred during the past decade as the result of increasing demand for labor, and of unionization and legislation, there has developed within the industry a definite trend toward reappraisal of its processing methods, with a view to reducing labor requirements. To date, this trend has been directed primarily toward refinements of present methods and more effective utilization of labor rather than toward a fundamental change in types of equipment. The latter, however, is under serious study by a number of mills.

3. Excess Capacity

The fact that the crushing industry as a whole operates only about one-third of the year has led some writers to the conclusion that the industry

[20] Computed from *Manufactures, 1939*, Sec. 2, Part 1, 16th Census of the U.S., 1940.

[21] No attempt is made here to evaluate such claims. The relative advantages and disadvantages of the several methods of oil extraction are discussed elsewhere.

is one of excess capacity and excessive costs.[22] This question obviously could be argued indefinitely, depending upon each individual's definition of "excessive." In any consideration of the cost of seasonal operations, it is necessary to take into account two factors. First of these is that the industry operates on a 24-hour basis with its plants running 144 or 168 hours per week. Thus a crushing mill that operates for 13–15 weeks out of the year utilizes its capacity to a greater extent than a plant or other business that operates 40 hours per week every week in the year. The latter is not necessarily assumed to have excess capacity and excessive costs, even though its capital equipment is idle more than 75.0% of the total available working time.

4. Alternatives in Operating Schedules

(a) Continuous Operation during the season vs. Intermittent Operation. The second factor to be taken into account in considering the cost of seasonal operations is the cost of alternative operating schedules. A mill, presently operating three months of the year, can extend its crushing season to twelve months by adopting the 40-hour week. One advantage that should accrue from such a change would be an increase in labor efficiency. The productivity of a single crew employed the year round could be raised above that of two or three crews on a seasonal basis. On the other side of the ledger would be an increase in certain costs. Twelve months' operation would require the installation of considerable additional storage capacity. It would also involve certain losses through the deterioration of seed in storage. These would vary from mill to mill and season to season depending upon the condition of the seed when received. A single-shift operation would also involve some loss in product income, since it is generally recognized that the yield of oil is lower when presses are cold and a single shift would require the mill to start each day's operations with cold presses. While data on the subject are not available, it appears that a 40-hour weekly operating schedule would increase rather than decrease the cost of crushing cottonseed. Obviously, such a schedule would in no way increase the utilization of capital equipment other than storage capacity.

(b) Seasonal vs. Continuous Year-Round Operation. Another method of solving the problem of seasonal operations is for a mill to secure sufficient seed to operate all year on a 24-hour basis. A number of mills, strategically located from the standpoint of seed supply, presently operate on such a schedule. Year-round operation on a 24-hour basis involves some of the same costs as a single-shift operating schedule. It requires storage capacity sufficient to handle the year's supply of seed which is normally

[22] J. S. Burgess, Jr., "Crushing Cottonseed Cooperatively," *Farm Credit Administration Circ.*, **No. C-114** (June, 1939).

received by the mill in about three months. It also involves some losses in seed deterioration. Despite the improvements that have been made in storage facilities, mills operating throughout the year frequently incur rather substantial losses as a result of the spoilage of seed in storage. On the other hand, year-round operation on a 24-hour basis significantly reduces many items of overhead cost. It also tends to increase labor efficiency by reducing turnover. Based upon the experience of mills operating on such a schedule, these savings more than offset the additional costs involved.

The fact that year-round operation has proven more economical in the case of a few mills does not necessarily mean that it is applicable on an industry-wide basis. Assuming no substantial increase in cottonseed production, year-round operation on an industry basis would involve a considerable further reduction in the number of mills and the centralization of the crush in a relatively small number of strategically located plants. This would result in an increase in the cost of transporting seed to the mills. Since a large proportion of the production of meal and hulls is consumed in the areas where mills are now located, there would also be an increase in transportation costs on products. The advantages and disadvantages of the present industry structure, as compared with a small number of centrally located mills operating on a 24-hour basis throughout the year, have not received sufficient study to warrant any definitive conclusions. The fact that a number of mills, operating a relatively short season, are able to compete successfully with mills that operate throughout the year indicates that all the advantages do not lie with the latter, even though they theoretically occupy the more favorable position.

IV. Marketing and Utilization of Cottonseed Products

A. Standardization of the Different Products

The four products of the cottonseed crushing industry are, in themselves, undifferentiated and the industry in general has made little effort toward product differentiation. On the contrary, most of the industry's efforts in the field of marketing have been directed toward standardization of products. As early as 1898, the Interstate Cotton Seed Crushers' Association adopted the first industry-wide standards for oil and meal.[23] These original standards, somewhat crude in the light of today's knowledge, have been regularly expanded and improved. Once each year, the Committee on Rules of the National Cottonseed Products Association (successor to the Interstate Association) meets to consider proposed changes in product standards and other trading rules. This Committee is made up of approxi-

[23] Interstate Cotton Seed Crushers' Association, *Constitution and By-Laws with Rules Governing Transactions in Cotton Seed Products*, as amended and adopted at annual meeting at Atlanta, Ga., July 21–22, 1898.

mately equal numbers of buyers and sellers of cottonseed products. Changes involving methods of chemical analysis must be referred to a Chemists' Committee before presentation to the Committee on Rules. Changes approved by the latter Committee must be adopted by the annual convention of the Association, which is composed of approximately 90% of the industry, both in number of mills and volume of business.

1. Standards for Oil

Under present standards, crude cottonseed oil is sold on the basis of three factors: color, flavor and odor (combined), and refining loss. Color and refining loss are subject to exact measurement. Flavor and odor are subjective qualities but a limit, in the form of the free fatty acid content of the oil, is placed upon the extent to which individual judgment may be exercised in their determination.[24] All crude cottonseed oil is sold for cash. Except in California and Arizona,[25] it is sold f.o.b. the mill. The seller guarantees weight and quality at destination but is not responsible for risks in transit unless he has improperly loaded and/or sealed the tank cars. The latter are furnished by the buyers. A considerable volume of oil is normally sold through brokers. Prices for oil in the various markets are published daily. No attempt is made to differentiate the product of individual mills, and competition is on the basis of price.

2. Standards for Cake and Meal

Cottonseed cake and meal are sold on the basis of protein content, which may be measured with exactness. In addition to the standards set up by the industry, many of the states have established cottonseed meal standards based upon protein, fat, fiber, and carbohydrate contents. Like oil, cake or meal is sold for cash, usually f.o.b. the mills. Most meal is packed in 100-pound sacks, although some of it is sold bulk, in carlots, to plants that process it further. Since 1926, the industry's trade association has carried on an industry-wide promotion and advertising program to promote the sale of cottonseed cake and meal. This program is based upon standardization of product. A few mills have sought to differentiate their cake and meal through the medium of branding and attractive packaging. With the industry's program of standardization and state requirements as to standards and labeling, this practice has not been widespread. Its advantage has been the creation of a repeat demand for the branded product rather than the enhancement of its price.

[24] National Cottonseed Products Association, *Rules,* 1945–46, p. 75.

[25] Mills in the Far West generally put their oil through the first refining process and sell semirefined oil on a delivered basis, usually to Los Angeles or to Berkeley, California.

3. Standards for Hulls

Cottonseed hulls have lent themselves to standardization less readily than any other product of the industry. Standards are based almost entirely on subjective qualities—color, odor, and freedom from foreign matter—without provision for specific measurement of these qualities. Despite this lack of standardization, no effort has been made by individual mills to differentiate their hulls. The product is sold for cash, f.o.b. the mill, either in bulk or in 100-pound sacks.

4. Standards for Linters

Except in the case of sales to the chemical industry, standardization of cottonseed linters has made only limited progress. Specific and generally satisfactory standards have been developed for linters sold to the manufacturers of chemical pulp. They provide for a cellulose content of 73.0% as a basis, with premiums and discounts for each 1.0% of cellulose above or below the base. Cellulose content is exactly measurable by chemical analysis.

No generally satisfactory standards have been developed, however, for the approximately 60% of linters production that is normally sold to buyers other than those representing the chemical industry. The industry's *Rules* provide only that linters made from burned or damaged seed that carry an objectionable odor or that contain excess foreign matter may be rejected if delivered on a contract. The United States Department of Agriculture in 1926 established a set of standards for linters.[26] These standards classify linters into 7 grades (with subgrades) according to staple, color, foreign matter, and area of production. In practice, linters can be graded according to these standards only on the basis of the subjective quality of appearance. For this reason, the federal standards have been used in trading only to a very limited extent.[27]

Most linters, other than those destined for the chemical industry, are normally sold on the basis of actual sample. Each transaction is the result of bargaining between buyer and seller. Like other cottonseed products, linters are sold for cash, f.o.b. the mill. They are packed in 600-pound bales. A few mills have established a reputation for producing superior quality linters and have been able to obtain above-average prices for their product. Generally, however, linters are undifferentiated, and competition, while by no means perfect, is the determinant of price.

[26] G. S. Meloy, "Development and Use of Standards for Grade, Color, and Character of American Cotton Linters," *U.S. Dept. Agr. Misc. Pub.*, **No. 242** (1936).

[27] Until the advent of price control, use of the federal standards was optional. Since Aug. 5, 1942, the Office of Price Administration has required that linters be sold on the basis of federal standards. A number of protests against this requirement have been registered and it is likely that, when price control is lifted, the industry will resume its usual methods of trading.

B. Marketing of Oil

1. Practices in Marketing and Utilization of Oil

The four products of the cottonseed crushing industry enter widely different markets. Cottonseed oil is predominantly a food oil. During World War II, its use in products other than foods was prohibited. Even in the absence of wartime restrictions, however, about 90% of crude oil production and practically 100% of refined oil production enters into food products. Normally, only off-grade oil and the foots remaining from the refining process are used in nonedible products.

Crude oil is sold by the mills to refiners. Its movement from the mill to the refinery is seasonal in nature, following closely the monthly volume of seed crushed. There are several reasons for this seasonal movement. First, is the fact that crude cottonseed oil is a perishable product. Its storage over any considerable period of time may result in quality deterioration and loss.[28] For this reason, most mills have not equipped themselves with extensive oil storage facilities. They ship oil at approximately the same rate they produce it; in fact, they must do so in order to operate at capacity during the crushing season. Financing is another factor contributing to the seasonal marketing of crude oil. Most mills borrow a part of their operating capital from the banks. Whether such capital is borrowed or taken from the mill's own funds, sound financing requires that products be marketed rapidly to minimize the risk of inventory losses. Lending agencies generally insist on such a practice. One further factor helps to explain the seasonal movement of crude cottonseed oil. Seasonal variation in consumer demand for finished fats and oils products corresponds generally to seasonal variation in the production of cottonseed oil. October, for example, is the month of peak consumption of edible fats, as well as the peak month of cottonseed oil production. Edible fat consumption does not vary during the year as widely as oil production, with the result that refiners perform the function of storing and financing a significant part of the cottonseed oil supply for several months each year.

The principal finished product made from cottonseed oil is vegetable shortening. In 1944, 45.7% of the refined cottonseed oil consumed entered this particular market.[29] Margarine absorbed an additional 20.0% of the cottonseed oil consumed in 1944, and 33.8% entered "other edible products." This latter classification includes salad and cooking oils, mayonnaise and salad dressing, bakers' and confectioners' fats, and oil used in packing

[28] It is recognized that a high-quality crude may be stored several months without significant deterioration. The danger of spoilage is always present, however, and few mills care to take the risk involved.

[29] U.S. Bureau of the Census, *Animal and Vegetable Fats and Oils, Calendar years 1940–44.*

certain canned food products. Only 0.5% of 1944 cottonseed oil consumption was accounted for by inedible products.[30]

2. Cottonseed Oil in Competition with Other Fats

In each of the foregoing product markets, cottonseed oil has numerous competitors. In 1940, the last prewar year, the Census Bureau reports 16 different fats and oils used in the manufacture of shortening.[31] Ten different oils were consumed in the manufacture of margarine, and 15 varieties were used in other edible products. The number of fats and oils used in these various products tends to minimize the range of potential competitors of cottonseed oil. There are hundreds of sources of fats and oils, ranging all through the animal, marine, and vegetable kingdoms. While no two fats or oils are identical in composition, considerable substitution is possible. Such substitution may be partial or complete. The manufacturer selects the oil or oils to be used in his finished product on the basis of physical and chemical characteristics, availability, and price. He may and frequently does vary his formula with changes in the availability and prices of particular oils. The use of cottonseed oil is determined by its relationship to competing commodities in terms of the above three factors.

For many years, cottonseed oil occupied a dominant position in the American market with respect to each of the foregoing three factors. The supply was considerably greater and the price generally lower than that of competing domestically produced oils. The factor of quality will be discussed elsewhere but it may be pointed out that, other factors being equal, manufacturers have generally preferred cottonseed oil for most edible products. The principal competition encountered by cottonseed oil was from imported oils, principally coconut, palm, and palm-kernel, and from lard.

This situation has changed considerably in the past 10 to 15 years with the rapid increase in soybean oil production. In 1930, only 14.4 million pounds of soybean oil were produced in the United States. By 1935, production totaled 105.1 million pounds. In 1940, the output was 533.2 million pounds, and the 1944 soybean oil production of 1,245.9 million pounds exceeded that of cottonseed oil. This development has significantly altered the competitive position of cottonseed oil. Whereas it formerly accounted for more than 80% of the fats and oils used in the manufacture of shortening, it supplied only 37.4% of that market in 1944. On the other hand, cottonseed oil has increased its share of the margarine market from 9.1% in 1933 to 45.2% in 1944. During the same period, it has increased slightly its share of the "other edible products" market. Thus it has demonstrated

[30] Percentages are figured on a refined oil basis. The foots or refining residue are used in nonedible products, primarily soap.

[31] "Other vegetable oils" and "fish oils" are considered as if each were a single oil.

a degree of versatility that, from the viewpoint of its producers, is fortunate.

On the finished product level, lard has historically been the principal competitor of cottonseed oil. With shortening providing the major market outlet for the oil, this relationship continues. Shortening must compete with lard in consumer markets, since both products serve the same end uses. In the form of margarine, cottonseed oil also competes with butter on the finished product level. In this market, competition has been greatly restricted by the legislative restrictions placed upon margarine. These restrictions have effectively prevented the yearly per capita consumption from rising much above 3.0 pounds, except during World War II. Consumer demand for these edible fats and oils products—lard, shortening, margarine, and butter—has been relatively inelastic. Consumption has increased at a slow, steady rate that appears to be more closely related to the growth of population than to any other factor.[32] Price competition is continuously present and, in periods when supplies are large, it is the dominant factor in the market.

C. Marketing of Cake and Meal

1. Cake and Meal Marketing Practices

In contrast to oil, which is marketed exclusively as a semifinished material, a large proportion of the output of cottonseed cake and meal is marketed as a finished product. Cake or meal is used principally as a livestock feed. Between 5 and 10% of production is normally used for fertilizer—either directly or in mixtures—while 90–95% is used for feeding. Three general methods of distribution have been employed by the mills. First of these is the mill-door sale, which is fundamentally a retail transaction, involving quantities ranging from one or two sacks up to 10 tons, and sometimes more. Most of the buyers are feeders located in the mills' respective trading territories, although some mill-door sales are made to retail feed stores and to local feed mixers. Since the mill performs the retailer's function in this type of sale, it generally obtains a somewhat higher price than on sales in carlots. While the differential varies with local conditions and sometimes with the type of customer, most mills realize about $3.00 per ton over the carlot price on their mill-door sales. This type of distribution has been increasing in importance. It has been encouraged by the industry's cake and meal promotion program, which is built upon showing the feeder how to use cottonseed meal in conjunction with his home-grown grains and roughages. In the 1940–41 season, 44.0% of cottonseed cake and meal production was sold at the mill door.[33]

[32] U.S. Bureau For. and Dom. Commerce, *Fats and Oils,* Nov., 1945.

[33] Based upon a survey by the National Cottonseed Products Association, April, 1943.

The second method of cake or meal distribution is through the dealer. The meal dealer buys from the mill in carlots and resells in the same quantity. He normally does not handle the product but arranges for direct shipment from mill to consumer. A few dealers also operate grinding plants where they produce meal or sized cake from purchased slab cake. The dealer performs the functions of finding a market for the product and of carrying any credit risks that may be involved. The latter are not normally great since the dealers sell principally to large feeders and feed dealers located outside the cotton-producing areas and to mixed feed and fertilizer manufacturers. The dealer has regularly handled a large proportion of the meal produced in certain surplus areas, particularly the Mississippi Valley States.

A few mills have developed direct sales organizations serving the same type of consumers as the dealer. Generally, this method of distribution is not practicable except for a large mill or group of mills. It has been employed principally in the western States. All mills use more than one method of distribution. Emphasis varies primarily as the result of differences in location.

Distribution of cottonseed cake and meal is seasonal in nature. Monthly sales correspond very closely to monthly production for much the same reasons as were previously outlined in discussing the seasonal movement of oil. Seasonal consumption of cake and meal corresponds more closely to production than does that of oil. The livestock feeder's requirements of protein are highest during the fall and winter months. It is during this season that large numbers of beef cattle are moved to the feed lots for finishing (primarily on corn and protein concentrates). Beef cattle that are wintered on the range and dairy cattle need increased quantities of protein to carry them through the winter in satisfactory condition. In much of the western range country, feed supplies must be delivered before the heavy snows interfere with transportation. With the coming of warm weather and the availability of pastures, the need for protein supplements declines sharply. This seasonal demand for cake and meal is a factor contributing to seasonal production.

2. Cake and Meal in Competition with Other Animal Feeds

Cottonseed cake and meal compete directly with other protein concentrates, chief of which are linseed meal, peanut meal, and soybean meal. Certain chemical differences exist between these four commodities but, essentially, they are interchangeable. Feeders can vary their feeding formulas in accordance with the availability and price of the various concentrates. For many years, cottonseed meal occupied a position in the American market similar to that of cottonseed oil in that its supply far exceeded—and its price was generally lower than that of any of its direct competitors.

Linseed meal was the only other protein concentrate available in significant quantity. Peanut meal was produced on a small scale. The decade beginning in 1930 witnessed a rapid expansion of soybean meal production, centered in the Midwest where large quantities of cottonseed meal had formerly been marketed. Production of soybean meal exceeded that of cottonseed meal for the first time in the 1941–42 season, and in 1944–45 totaled 3.6 million tons,[34] compared with 1.9 million tons of cottonseed meal produced during the same season. This increase in soybean meal production has been accompanied by a narrowing of the differential between its price and that of cottonseed meal. In 1929, the latter sold at Memphis for $16.00 less than soybean meal in the Midwest. At the present time, the two commodities sell at approximately the same price in their respective areas of production.[35]

In addition to the competition of other protein concentrates, the demand for cottonseed meal is also influenced by the supply of such commodities as corn, wheat, oats, mill feeds and even some types of hay. Under certain market conditions, cottonseed meal can be used economically to replace such commodities (and *vice versa*) in livestock rations. Like oil, cottonseed meal moves into a market where many alternative commodities are normally available and where competition is based primarily on price. Unlike edible fats and oils, the demand for protein concentrates appears to be elastic as indicated by the large increase in consumption in recent years, even prior to the abnormal wartime demand.

D. Marketing and Utilization of Hulls

Cottonseed hulls might well be termed the "orphan" product of the industry, since most mill managers have devoted less effort to the marketing of hulls than to any other product. The original use of hulls was as a fuel. Many of the early writings on the industry contain computations of the value of hulls in terms of fuel for mill operation.[36] Even in recent years, hulls have been burned under mill boilers during periods of very low prices. Today, however, most hulls are used as a feed for livestock. Unlike cake or meal, hulls are a roughage rather than a protein concentrate. They are comparable in feeding value to good-quality grass hay. In this field, they possess certain advantages in that they can be fed with a minimum of waste and, in many sections of the Cotton Belt, they cost less than hay.

Like oil and meal, hulls are marketed seasonally. Since they are the

[34] U.S. Bureau of Agricultural Economics, *The Feed Situation,* Oct., 1945.

[35] Memphis, Tenn. and Decatur, Ill. are the principal points for which prices are regularly quoted. It should be noted that, in 1929, production of soybean meal was negligible. The price differential at that time is therefore not as significant as might be inferred from the absolute figures.

[36] See D. A. Tompkins, *Cottonseed Oil,* 3rd ed., D. A. Tompkins, Charlotte, N. C., 1904.

least valuable of cottonseed products, mills generally have not provided extensive hull storage facilities. They sell and ship their hulls only slightly less rapidly than they produce them. Because of their bulkiness, it is generally impracticable to ship hulls for long distances. In some seasons, limited quantities of hulls move from the Valley States into the Southeast and/or Southwest. The greater proportion of hull production, however, is sold locally. Most sales are made directly to feeders, although some hulls move to mixed feed manufacturers.

Chemically, hulls appear to have possibilities as an industrial raw material. During World War II, substantial quantities were consumed in the manufacture of furfural, a selective solvent having varied applications in the chemical industries. Some success has also been achieved in the production of a plastic compound containing a large percentage of hulls.[37] The market for hulls as an industrial raw material appears capable of considerable future expansion. For the present and some time to come, however, the value of hulls will be determined primarily by the demand for roughage feeds.

E. Marketing and Utilization of Linters

Cottonseed linters enter a wider variety of end-use markets than any other cottonseed product. It would be impracticable to analyze the many factors that influence supply and demand in each of these markets, and discussion will necessarily be confined, as much as possible, to the raw material. Products made from linters may be classified into three broad groups: (*a*) those in which linters are used in substantially their original form, (*b*) those in which linters are changed physically by spinning, and (*c*) those that involve both physical and chemical change.

The first group includes: products of the bedding industry, where linters are used as a filler for mattresses and comforts; automobiles and furniture, in which linters are used, also as a filler, for upholstery; and several miscellaneous items. Their principal competitor in this field is cotton waste, a by-product of the textile mills. In certain individual product markets within this group, linters also encounter competition from such materials as sponge rubber, cotton, moss, sisal, flax tow, and kapok. While each of these raw materials possesses individual characteristics, a considerable degree of interchangeability is always present, especially between linters and cotton waste, and price competition is active.

The second group of products includes yarns, twine, wicks, carpets, mops, and surgical dressings in the production of which spinning is necessary. Only the best grades of linters enter this market. The principal competition in this field comes from cotton waste and the lower grades of

[37] F. Rosenthal, *Manufacturers Record,* Feb., 1941.

cotton. During the 1930's, the foregoing two groups of products accounted for about 50% of the domestic consumption of linters.

The remainder of domestic linters consumption is normally accounted for by products in which the physical and chemical character of the raw material is changed. Chief of such products are rayon, plastics, lacquers, and explosives. Before entering such products, linters are purified—that is, they are reduced to a pulp that analyzes approximately 98.0% α-cellulose. In this form, linters chief competition is from wood pulp. Generally, linter pulp is higher in cellulose content and is whiter than wood pulp. It is also more resistant to certain types of undesirable chemical reaction.[38] On the other hand, wood pulp is substantially lower in cost than linter pulp and its price is much more stable. This latter factor is significant for it enables the manufacturer, who uses wood pulp, to determine his raw material costs for considerable periods in advance, whereas the price of linter pulp fluctuates frequently in accordance with changes in the price of linters. Generally, it may be said that linter pulp holds the advantage in products that must meet rigid specifications, whereas wood pulp is preferred in products where price is the primary consideration. It should be observed that the quality of wood pulp has been consistently improved. The history of competition between these two materials reveals a tendency for wood pulp to move gradually into markets that were originally developed with the use of linter pulp.

Like that of other cottonseed products, the marketing of linters is seasonal in nature. Monthly shipments from the crushing mills follow monthly production very closely. Two general methods of marketing are used by the mills: (*a*) direct sales, and (*b*) sales to dealers. All linters for chemical purposes are sold directly to the pulp plants. Most linters destined for other uses are sold to dealers, who in turn resell to consumers. The linter dealer performs much the same services as the cotton merchant. He assembles varying qualities of linters and attempts to meet the consumer's demand for lots of relatively uniform quality. To some extent, the dealer also performs the function of financing, since he generally carries for his own account a certain quantity of linters.

The demand for linters is closely related to gross national product.[39] During periods of high industrial activity, the production of linters is readily absorbed. During periods of depression, it has been difficult to market linters at any price. While markets for linters appear capable of expansion, such expansion must cope with stiff price competition at both the raw material and the finished product levels. The industry can prob-

[38] R. F. Conaway, *Ind. Eng. Chem.*, **30**, 516–523 (1938).

[39] "Gross national product" is defined as the total value of goods and services produced in the United States.

ably best meet this competition by capitalizing upon the inherent quality characteristics of its product.

V. Price Structure

As indicated in the foregoing section of this chapter, price plays a major role in the cottonseed products industry. Each of the cottonseed products markets is characterized by the presence of price competition. Product prices determine the gross income of the crushing mills and this income, in turn, controls the prices paid by the mills for seed. Cottonseed prices, for their part, are a measure of the farmer's income and are therefore important, both economically and politically.

The prices of cottonseed products are influenced by four major factors: (*a*) movements of the general price level, (*b*) the volume of cottonseed products production, (*c*) the production of competing commodities, and (*d*) demand. These factors are obviously intermingled and their relative importance is by no means constant. During certain periods, supply has dominated the market. During other periods, the general price level appears to have exerted the strongest influence upon cottonseed product prices.

A. Relation of Oil and Meal Prices to the General Price Level

The relationship of oil and meal prices to the general price level from 1931 through 1940 is shown in Figure 177. This chart is based upon three series of index numbers of wholesale prices, representing all commodities, crude cottonseed oil, and cottonseed meal. The "all commodities" index is that of the Bureau of Labor Statistics, transposed to an August, 1926–July, 1927 base, to conform to the cottonseed crop year. The oil index is based upon the price of crude oil, f.o.b. southeast mills, and the meal index represents the wholesale price of meal at Memphis.

A general tendency for the prices of oil and meal to move up and down with the general price level is evident. That this relationship is far from perfect is indicated by the fact that cottonseed product prices vary much more widely than does the general price level and that they sometimes move in the opposite direction. The price of cottonseed oil, for example, moved with the general price level 15 times out of a possible 19 during the period shown. Cottonseed meal prices appear to be influenced somewhat less by general price changes. They moved with the all-commodities index only 12 times out of a possible 19. The comparable figures for hulls and linters (not shown in the chart) were 12 and 10, respectively.[40] The substantially greater range of fluctuation in cottonseed product prices, compared with the general price level, is the result of several factors. First, it

[40] Because the much wider range in their prices would distort the chart, data for hulls and linters have not been included in Figure 177.

should be noted that the Bureau of Labor Statistics' all-commodities index is a composite of nearly 900 price series in which increases and decreases are partially compensating. Such an index might therefore be expected to vary less than the price of an individual commodity. Second, the index is

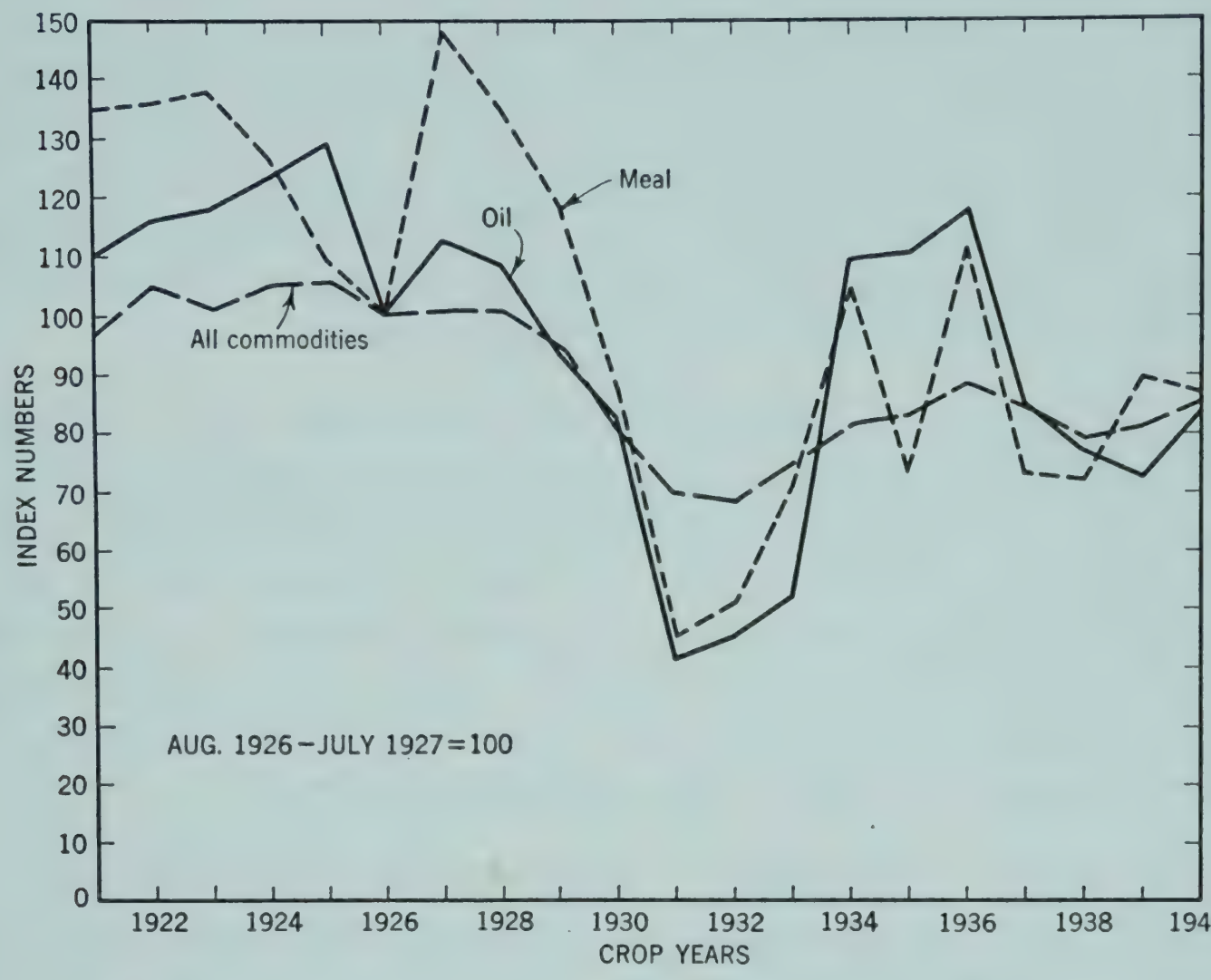


Fig. 177. Index numbers of wholesale prices: all commodities, cottonseed oil, and cottonseed meal, crop years 1921–1940.

based upon a wide variety of commodities, ranging from raw materials to finished durable goods. It is generally recognized that the latter vary less frequently and less widely in price than the former. Cottonseed oil and meal may be classified as semifinished materials and would therefore be expected to be more variable than the all-commodities index. Finally, cottonseed products prices vary more widely than the general price level because of the influence of factors other than general price movements.

B. Prices of Cottonseed Products in Relation to Volume of Production

One of the factors influencing the prices of cottonseed products is the volume of production of these products. As pointed out previously, the quantity of cottonseed produced and crushed depends primarily upon the size of the cotton crop; and the quantity of products produced is adjustable to market conditions only to a very limited extent. This fact has led some writers to the conclusion that the production of cottonseed products

is the dominating influence upon price.[41] Superficially, such a conclusion appears warranted. A simple comparison of the production and price of each cottonseed product brings out sharply the inverse relationship between the two series; in fact, it exaggerates it. Such a comparison is somewhat misleading, however, in that it tends to attribute to production the influence of other factors.

In an attempt to evaluate roughly the influence of production upon price, coefficients of correlation between the production and price of the four cottonseed products have been computed for the period 1921 through 1940.[42] These are presented in Table 176. To minimize the influence of changes in the general price level, product prices were deflated by the Bureau of Labor Statistics' index of wholesale prices.

1. Price vs. Production of Hulls

It will be noted in Table 176 that the highest degree of inverse relationship between production and price exists in the case of hulls, in which the coefficient of correlation is -0.77 with a probable error of ± 0.06. This relatively close relationship is supported by inductive analysis. Since the market for hulls is limited, both as to variety of uses and geographically, production would be expected to exert a greater influence upon their price than upon the prices of other cottonseed products.

2. Price vs. Production of Cottonseed Oil and Competing Fats

In the case of oil, the coefficient of correlation between production and price during the 1921–40 period was -0.40, ± 0.13. This is a relatively low degree of relationship and indicates that other factors are more significant than the production of cottonseed oil in the determination of its price. One of the most important of these other factors is the total production of edible fats and oils within the United States. The relationship of such total production to the price of cottonseed oil has been computed for the period 1924 through 1940.[43] During this period, the coefficient of correlation between the price and production of cottonseed oil was only -0.31, ± 0.15, indicating a low degree of relationship. The comparable measure of relationship between the price of cottonseed oil and the domestic production of edible fats and oils was -0.50, ± 0.12, indicating a marked degree of relationship. The foregoing measurements plus inductive analysis justify the conclusion that the production of domestic edible fats

[41] See, for example, W. Hamilton and associates, *Price and Price Policies*, McGraw-Hill, New York, 1938, p. 222.

[42] All data refer to crop years. These computations were not carried past the 1940 crop year because price relationships subsequent to that season have been distorted by wartime conditions. Most prices have been unchanged at ceiling levels since 1941 or 1942.

[43] This shorter period was used because edible fat and oil production data, beginning with the 1924 crop year, were readily available.

and oils is considerably more important than the production of cottonseed oil in determining the price of the latter. Supporting this conclusion, it may be noted that the relationship between the production and price of cottonseed oil was closer during the 1921–40 period than during that of 1924–40. This may be explained by the fact that cottonseed oil production represented a larger proportion of total edible fats and oils production during the earlier years of the interwar period than it did during more recent years.

In order to indicate the relationship that exists between the price of cottonseed oil and that of competing commodities, there has been included in Table 176 a computation of the coefficient of correlation between the price

TABLE 176

Coefficients of Correlation: Price and Production of Cottonseed Products, Price of Oil and Production of Edible Fats, Price of Meal and Production of Oilseed Meals, Price of Cottonseed Oil, and Price of Lard

Series	Period	Coefficient of correlation	Probable error
1. Production and price of cottonseed oil	1921–1940	−0.40	±0.13
2. Production and price of cottonseed meal	1921–1940	−0.46	±0.12
3. Production of principal domestic oilseed meals[a] and price of cottonseed meal	1921–1940	−0.39	±0.19
4. Production and price[b] of cottonseed hulls	1921–1940	−0.77	±0.06
5. Production and price[b] of cottonseed linters	1921–1940	−0.39	±0.13
6. Production and price of cottonseed oil	1924–1940	−0.31	±0.15
7. Production of principal domestic edible fats and oils[c] and price of cottonseed oil	1924–1940	−0.50	±0.12
8. Price of cottonseed oil and price of lard	1924–1940	+0.87	±0.04

[a] Includes cottonseed, linseed, peanut, and soybean meals.

[b] Satisfactory price series for hulls and linters are not available. In this instance, the average selling value of the two commodities, as reported by the Census Bureau, has been used.

[c] Includes corn oil, cottonseed oil, edible olive oil, peanut oil, soybean oil, oleo oil, edible tallow, edible stearin, and lard.

of oil and the price of lard. One writer[44] on the subject of cottonseed product prices concluded that there was very little relation between the prices of these two commodities. The coefficient of + 0.87, ± 0.04 indicates a very close positive relationship between the two. It is not to be inferred that the price of lard determines the price of cottonseed oil, or *vice versa*. It may properly be concluded, however, that the prices of these two commodities cannot deviate greatly from each other because both are influenced to approximately the same extent by changes in the general price level, by the production of edible fats and oils, and by demand.

[44] W. Hamilton and associates, *Price and Price Policies*, McGraw-Hill, New York, 1938, p. 212.

3. Price of Meal in Relation to Production

The inverse relationship between the production and price of cottonseed meal is somewhat closer than in the case of oil. The coefficient of correlation of $-0.46, \pm 0.12$ is indicative of a moderate degree [45] of relationship. Unlike that of oil, the price of meal is more closely related to meal production than to the total production of oilseed meals. This results, at least partly, from the fact that prior to 1934 cottonseed meal accounted for much the greater part of total oilseed meal production.

4. Price vs. Production of Linters

The degree of relationship between the production and price of linters, as indicated in Table 176, is very low. Two factors appear to be primarily responsible. First, the carryover of linters from years of large crops into years of short crops is relatively greater than that of other cottonseed products. Second, linters are an industrial raw material and, as such, are more strongly influenced in price by changes in industrial activity and the general price level than are other cottonseed products.

C. Analysis of Price Variability in Cottonseed Products

One of the outstanding characteristics of cottonseed product prices is their variability. That oil and meal prices vary much more widely from year to year than the general price level was shown in Figure 177. The prices of hulls and linters are even more variable than those of oil and meal. Numerous methods may be employed to measure price variability. Mills [46] has developed three of the most useful, namely, a measure of monthly variability, a measure of annual or year-to-year variability, and a measure of the frequency of monthly price changes. These three measures have been computed for cottonseed oil, cottonseed meal, and certain competitive commodities, and are shown in Table 177.

All the commodities listed in Table 177 exhibit a degree of variability that is relatively high. The monthly variability of cottonseed oil and meal prices is slightly, but not significantly, lower than that of competing commodities. It is quite possible that this lower degree of intraseasonal variation results from the greater availability of market information relating to these two commodities. Once the size of the cotton crop is known, the supply of cottonseed products can be estimated within reasonable limits. Such estimates can be revised monthly on the basis of Bureau of the Census reports of production and disappearance. Such detailed information is not generally available for competing commodities. The

[45] According to the classification of R. E. Chaddock, *Principles and Methods of Statistics,* Houghton Mifflin, Boston, 1925, p. 304.

[46] F. C. Mills, *The Behaviour of Prices,* National Bureau of Economic Research, New York, 1927.

TABLE 177

Variability of Prices of Cottonseed Oil and Meal and Certain Competing Commodities, 1929–40 Crop Years

Commodity	Monthly variability[a]	Annual variability[b]	Frequency of monthly price change[c]
Cottonseed oil	10.0	24.1	0.965
Corn oil	11.1	26.4	0.888
Peanut oil	10.6	20.0	0.846
Soybean oil	12.4	25.9	0.860
Lard	11.0	27.9	0.986
Cottonseed meal	8.5	29.8	0.993
Soybean meal	11.6	21.8	0.972

[a] Mean deviation from average annual price expressed as a percentage of the average annual price.
[b] Mean deviation (from the mean) of link relatives of average annual prices.
[c] Ratio of number of monthly price changes to maximum possible number of changes.

price of cottonseed meal varies somewhat less from month to month than does that of oil. This tends to support the previously discussed finding that the price of meal is more closely dependent upon production than is that of oil.

In terms of year-to-year variability, cottonseed oil prices exhibit no characteristics that distinguish them from the prices of competing commodities. In fact, cottonseed oil falls at almost exactly the midpoint of the range of variation of the fats and oils prices shown in Table 177. The price of cottonseed meal has varied more widely from year to year than has the price of soybean meal, its principal competitor. Here again the influence of production appears to have been active. During the period covered, the production of soybean meal has steadily increased. Production of cottonseed meal, on the other hand, has fluctuated quite widely.

With respect to the third measure of price variability—frequency of monthly price change—cottonseed products and competing commodities rank very high. Cottonseed oil is higher than any of the fats and oils analyzed except lard. Cottonseed meal prices have changed more frequently than those of soybean meal. Frequency of monthly price change is indicative of the extent to which prices are administered or controlled. The high frequency of change in cottonseed oil and meal prices supports the observation made in the section on marketing that price competition is highly active in the markets for these commodities.

D. Seed Prices

1. Seed Prices in Relation to Mill Operation

Discussion thus far has been concerned with the characteristics of cottonseed product prices. These prices, determined as they are in highly

competitive markets, set a general limit to the price which the crushing mills pay for cottonseed. Given the prices of cottonseed products and knowing the probable yield of each product from a ton of cottonseed, it is a simple matter for the mill to compute the gross value of a ton of seed in terms of products. Next, the mill estimates its crushing costs, also on a per ton of seed basis. To its cost, the mill adds such profit as it desires or hopes to make and subtracts the total from the gross value of products. The result is, theoretically, the price that the mill will pay for seed.[47]

An offering price for cottonseed, arrived at in the above manner, is subject to considerable modification. Since the volume of seed crushed by a mill influences its per ton costs, such a price depends in part upon the size of the crush. Of even greater significance, such a price must be adjusted to meet the realities of competition in the cottonseed market. Determination of a seed price by the foregoing method is no assurance that the mill can buy seed at the computed price. Mill *A*, for example, may estimate that, on the basis of product values, a buying price of $40.00 per ton [48] for seed will enable it to cover costs and earn a satisfactory profit. However, if mill *B* offers $41.00 per ton in the same area, mill *A* will have to meet the higher price or lose seed. Because of imperfections in the market, this adjustment is not always automatic and immediate, but no mill can buy seed over an extended period at prices below those of its competitors.

This competition among the mills is the outstanding characteristic of the cottonseed market. Earlier in this chapter, it was pointed out that the capacity of the industry is considerably greater than the quantity of seed available each year for crushing. Also, approximately 50% of the costs incurred in crushing cottonseed [49] are in the nature of overhead expenses, the amount of which is relatively constant regardless of the quantity of seed crushed. The greater the volume of seed crushed, therefore, the lower such overhead costs will be per ton. With capacity available and with the possibility of reducing overhead costs by crushing a larger volume, each mill aggressively seeks to purchase the maximum volume of seed. With supply limited and each mill seeking the largest possible share, the market for cottonseed is distinctly a sellers' market.

2. Practices in Seed Marketing

As noted previously, most of the cottonseed crop is sold by the farmer to the ginner who, in turn, sells it to the crushing mill. Cottonseed are

[47] For a detailed description of this process, see K. Y. Sidall, *National Association of Cost Accountants' Bull.*, **16,** No. 8, 421–433 (1934).

[48] These prices are purely examples and have no relation to currently prevailing prices. Cottonseed in February, 1946 brought a minimum price of $55.00 per ton.

[49] Reference is made here to conversion costs, excluding the cost of seed and of seed transportation.

purchased by the mills on an f.o.b. basis, that is, the mill offers a uniform price f.o.b. the gin and pays the cost of transporting seed to the mill. Transportation costs from varying points are averaged. This method of pricing is common to many commodity markets in which the buyer takes the initiative. It is employed in the sale of corn oil, cottonseed oil, peanut oil, soybean oil and other commodities. It is comparable to the method used by manufacturers who sell their products at a uniform delivered price regardless of destination. The f.o.b. method of pricing cottonseed has the advantage of simplicity. A mill can quote one price to all sellers, rather than a different price for each seller or a delivered price, which results in a different return to each seller. The f.o.b. pricing also extends the area in which each mill can compete in the purchase of seed. Under a delivered price system, a mill would be restricted to sellers within a limited area determined by transportation costs. Within that area, however, it would have to meet only such local competition as might exist, unless its price was considerably out of line with that prevailing at other delivery points. It would, in other words, have a certain advantage over the seller within its own trade area. Under the existing method of pricing, no mill possesses such an advantage. One mill may, and frequently does, go to the door of another mill to buy seed. Obviously, this practice involves a certain amount of cross-hauling which has been subject to some criticism.[50] Admittedly, cross-hauling adds to the cost of marketing cottonseed. The amount and incidence of this additional cost have never been determined. Judged by the standards of economic perfection, such additional costs are not justifiable. Since the realization of such standards does not appear imminent, the problem resolves itself into whether such costs are too high a price to pay for the competition that is fundamental to our existing economic system.

3. Farm Prices vs. Mill Prices of Seed

Satisfactory data on the prices paid for cottonseed by the crushing mills are, unfortunately, not available and it is necessary in analyzing cottonseed prices to use the farm price of seed. This has been a cause of confusion in that it has sometimes been assumed that the price received by farmers is equivalent to the price paid by the mills, and that the difference between the farm price of seed and the value of cottonseed products represented the mills' gross income.[51] Obviously, this is not the case since the mills do not generally buy seed directly from the farmer. One survey [52] in this field brought out the fact that, during the 1939–40 season, the

[50] E. G. Schiffman, *Vegetable Oil Mill Crushing Capacity and Probable Crush, 1942–43 Season,* Farm Credit Administration, W. C. 2, Oct., 1942.

[51] J. S. Burgess, Jr., "Crushing Cottonseed Cooperatively," *Farm Credit Administration Circ.,* **No. C-114,** 3 (June, 1939).

[52] Conducted by the National Cottonseed Products Association.

average mill f.o.b. price exceeded the average farm price by $5.28 per ton. Generally, the farm price is related to the mill price but this relationship is neither constant nor exact. At times and in certain areas, the farm price may equal or even exceed the mill price. At other times, it is substantially below it. Varying business policies of the gins, which purchase the seed from the farmer and resell them to the mill, account for these variations. The gin is a multiple enterprise. Normally, it performs the ginning service and purchases cottonseed. Frequently, it purchases cotton lint, sells feed products, and engages in other activities. One gin may offer a relatively high price for cottonseed in order to attract patronage. Another gin may use a low ginning charge for the same purpose. Such practices are comparable to use of the "loss leader" by the retailer to attract customers.

There is a general tendency for the farm price of cottonseed to increase as the season advances. This is illustrated in Table 178 which shows the

TABLE 178

Monthly Prices of Cottonseed, Cottonseed Oil, and Cottonseed Meal, 1930–39 Average[a]

Month	Cottonseed, dollars per ton	Cottonseed oil, cents per pound	Cottonseed meal, dollars per ton
August	21.40	6.30	25.32
September	20.95	6.01	23.33
October	21.59	5.93	22.68
November	22.53	6.06	24.13
December	23.07	6.21	23.96
January	23.34	6.28	24.04
February	23.82	6.32	23.55
March	24.20	6.39	23.65
April	24.52	6.24	24.37
May	24.63	6.15	24.14
June	23.66	6.08	22.89
July	23.07	6.29	24.73

[a] Computed from prices published monthly by U.S. Dept. Agr., as follows: cottonseed, average U.S. farm price; cottonseed oil, crude in tanks, f.o.b. southeastern mills; cottonseed meal, 41% protein, sacked, in carlots, f.o.b. Memphis.

average monthly farm price of seed and the price of oil and meal for the period 1930–39. During this period, the price of seed averaged $2.47 per ton higher during the last three months of the season than during the first three months. While there exists some tendency for cottonseed product prices to advance with the season, the rise in seed prices is largely the result of competition among the mills. As explained previously, a mill's original offering price for seed must be based upon an assumed quantity that it will crush. If it can purchase that quantity at a satisfactory price, each additional ton it can purchase will theoretically reduce its per ton overhead costs. Proceeding on that basis, mills tend to increase their buying prices as the season advances. While additional volume reduces

overhead costs per ton, such volume purchased at an increased price raises the average per ton cost of all seed crushed. Thus, if a large volume is purchased at the higher prices generally prevailing during the latter part of the season, any profit made on early season purchases may be wiped out. In practice, the bulk of the seed is purchased during the early months of the season. Late season prices, therefore, are not properly representative of any large volume of transactions.

4. Analysis of Seed Price Variability

Similar to that of most agricultural commodities, the price of cottonseed is highly variable. The three measures of variability, that were previously computed for cottonseed products and competing commodities (Table 177), have been computed for cottonseed and several of the most important agricultural commodities. These are shown in Table 179, which,

TABLE 179

Variability of Prices of Cottonseed and Several Major Agricultural Commodities, 1910–44

Commodity	Monthly variability[a]	Annual variability[b]	Frequency of monthly price change[c]
Cottonseed	8.1	27.7	0.995
Cotton	7.8	24.6	0.916
Wheat	7.5	21.4	0.885
Corn	10.3	24.4	0.885

[a] Mean deviation from average annual price expressed as a percentage of average annual price.
[b] Mean deviation (from the mean) of link relatives of average annual prices.
[c] Ratio of number of monthly price changes to maximum possible number of changes.

since the data were readily available, covers the crop years 1910 through 1944. Cottonseed prices show no outstanding characteristic in their month-to-month variation. Within the season, they are slightly more variable than those of cotton and wheat but somewhat less variable than prices of corn. From year to year, cottonseed exhibits a somewhat greater degree of variability in price than cotton, wheat, or corn. The wide fluctuation in cottonseed production appears to be the major factor responsible for this greater year-to-year variation. Competition for seed is also a factor since, in years of short production, it tends to push seed prices above the level that might be expected solely on the basis of the supply situation. The price of seed also shows a higher frequency of change from month to month than do the prices of cotton, corn, or wheat. With respect to this latter measure of variability, it should be noted that, over most of the past 15 years, the prices of cotton, corn, and wheat have been supported

by federal action.[53] A support price, if effective, tends to reduce the frequency of price change. This is probably partly responsible for the lower frequency of price change in cotton, corn, and wheat, as compared with cottonseed. The three measures of price variability do not indicate any marked differences in the price behavior of cottonseed, cotton, corn, and wheat. They do demonstrate a high degree of variability or flexibility in the prices of all four commodities and the absence of any significant degree of control by either buyers or sellers.

From the viewpoint of cotton producers, ginners, cottonseed crushers, manufacturers of finished products, and consumers, a greater degree of stability in the price of cottonseed and cottonseed products would probably be desirable. However, since cottonseed products and competing commodities are all of agricultural origin and consequently subject to relatively sharp changes in production volume, greater stability appears unlikely except through methods that would destroy free markets.

VI. Future of the Industry

The future of the cottonseed crushing industry depends not so much upon factors within the industry itself as upon developments with respect to cotton lint. It was pointed out previously that the industry's principal problem is obtaining an adequate supply of raw material, and that this supply of raw material is dependent upon cotton production.

A. Influence of National Cotton Policy

The future of American cotton production is today an unknown quantity. There is no lack of potential demand for American cotton both in this country and abroad. Neither is there any lack of desire on the part of farmers to produce cotton in substantial volume. Cotton yields a much larger gross income per acre than any other major field crop. The factor that will primarily determine whether the demand for cotton and the desire to produce it can be brought together is price.

With the exception of one year, the price of cotton lint has been "supported," since 1929, by a variety of federal programs including loans, production control, purchase, and holding operations.[54] While these programs may have afforded cotton producers some temporary relief from the very depressed conditions existing in the early 1930's, their net effect has been to weaken the position of American cotton in both domestic and foreign markets. Before World War II, a major portion of the export

[53] A government support price has been effective for cottonseed during World War II. This program was established to protect the support prices that had been set up for other oilseed crops.

[54] For a detailed discussion of the various federal cotton programs and their effects, see J. F. Moloney, *Cotton In Peace and War,* Vanderbilt Univ. Press, Nashville, 1944.

market had been lost to foreign producers, largely as a result of price support. With foreign cotton selling considerably under the supported price level for American cotton, it seems unlikely that exports can regain their former level (roughly 50% of production) without some change in national cotton policy. In domestic markets, cotton price supports have stimulated and encouraged the production and use of competitive commodities, especially the synthetic fibers and paper products. These developments point inevitably toward reduced cotton consumption with a consequent decline in production.

If the cottonseed crushing industry is to obtain a reasonably adequate supply of raw material from its usual source, a modification of existing national cotton policy is essential. Such a modification will not be made merely because it would be in the interests of the crushing industry. Any change in policy will have to serve the interest of the millions of farmers who depend upon cotton production for a living. The technical means for such a modification of national cotton policy are available. Existing knowledge in the field of cotton production definitely indicates that cotton can be produced in the U.S. at a cost that would enable it to compete advantageously here and abroad [55] and, at the same time, return an adequate income to producers. This is not to say that all farmers or all localities can produce at such a cost level. A revision of present policy to permit cotton lint to sell at a competitive price would make cotton production unprofitable in some areas and on some farms in most areas. Nevertheless, such a revision is clearly indicated as fundamental to the establishment of the economy of the Cotton States upon a sound basis.

B. Development of Alternative Raw Materials

In the absence of a change in present national cotton policy, the cottonseed crushing industry must look to other sources of raw material to keep its plants in operation. There are a number of such potential sources, including, but not limited to, soybeans, peanuts, flaxseed, sunflower seed, perilla seed, and castor beans. While all of these oilseeds can be produced in the area now served by the cottonseed crushing industry, it is immediately apparent that the production of some of them on a scale comparable to the capacity of the cottonseed crushing industry would result in a volume of products far in excess of the amount this country has ever consumed. Maximum consumption of castor oil, for example, was 186.5 million pounds in 1944, compared with 1,132.5 million pounds of cottonseed oil used in the same year. Consumption of sunflower and perilla oils is much smaller.

[55] See, for example, C. A. Bonnen and A. C. Magee, *Estimates of the Cost of Producing Cotton in Eight Selected Areas in Texas,* Progress Report 912, Texas Agr. Expt. Sta., 1944.

Peanuts are exclusively a southern crop and a good source of high-quality oil and protein. A number of cottonseed crushing mills crush peanuts regularly. The principal market for peanuts, however, is in the food and confectionery trades where they command a considerably higher price than can be paid by the crushing mills. As a result, the mills are able to obtain only a limited volume of "seconds" or surplus nuts which the primary market does not want.

Flaxseed is being produced on a very limited scale in the Cotton States and is being crushed in the cottonseed industry. Sufficient experience has not yet been accumulated to determine whether its production on a large scale is practicable. Consumption of linseed oil, however, has always been less than half that of cottonseed oil.

The marked expansion in soybean production during the past decade has taken place primarily outside the Cotton States. To date, soybean production has become established in the South only in limited areas of North Carolina, Arkansas, and Mississippi. This has been due partly to the difficulties encountered in developing varieties of the soybean adapted to southern climatic conditions and partly to the fact that any cash crop is at a disadvantage in competing with cotton for land. These difficulties, however, appear by no means to be insurmountable and it is quite possible that soybeans may in time become an important addition to the raw material supply of the cottonseed crushing industry.

One other potential source of raw material should perhaps be mentioned. Work has been carried on for several years looking toward the development of a variety of the cotton plant that would be grown for its seed [56] and would be planted, cultivated, and harvested in a manner similar to that of other oilseed crops and the grains. While conclusions regarding the potentialities of such a crop would at present be premature, progress to date has been encouraging.

Obviously, adequate raw materials supplies will not in themselves enable the cottonseed crushing industry to maintain or improve its position in the face of the competition it will undoubtedly encounter in the foreseeable future. The industry will have to keep its methods of processing and marketing on a par with those of its competitors. Uncertainty regarding the future supply of raw materials has acted as a deterrant to modernization and new investment. The industry has the advantage of favorable public acceptance of its products. With reasonable assurance of a future supply of raw materials, there is no reason why the cottonseed crushing industry should not progress as an important supplier of food, feed, and industrial raw materials.

[56] For an early report on this work, see D. T. Killough, *Lintless Cotton*, Progress Report 661, Tex. Agr. Expt. Sta., 1939.

E. UTILIZATION OF COTTONSEED PRODUCTS

CHAPTER XVII

PROCESSING OF COTTONSEED OIL

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The processing which crude cottonseed oil must undergo after it leaves the mills depends upon the finished products desired. A number of these products and the general process steps to be employed may be conveniently illustrated by the accompanying diagram (Fig. 178).

I. Refining

It will be noted that the first processing step is that designated as "refining." By refining cottonseed oil is meant the treatment of the crude material with a certain percentage of caustic soda solution varying in its sodium hydroxide content. The caustic combines with the free fatty acids of the crude oil to form soap, extracts the coloring matter by a selective solvent action, coagulates or destroys lipides and other minor constituents, and removes suspended foreign matter, such as traces of meal and gross dirt. The above material is thus rendered insoluble in the oil and is removed by gravity settling or otherwise. It is known as soapstock or foots.

A successful refining operation should give a maximum yield of refined oil, free from the major part of the coloring matter and nonfatty materials, excepting oil-soluble unsaponifiable matter, and containing no more than traces of free fatty acids.

The success of all subsequent processing steps depends upon the efficiency with which the refining has been carried out. Improper removal of color bodies and lipides will interfere with earth bleaching, and so forth. Refining losses, in excess of normal, raise the manufacturing cost on account of the differential in value between oil and soapstock, and the lowered yields of refined oil per unit of operation. Therefore, good refining may be said to form the cornerstone of successful cottonseed oil processing.

Many refining methods have been suggested and tested—some in lengthy commercial trials. Scores have been made the subject of patents, both U.S. and foreign. Any attempt to cover adequately the patented refining techniques would require a volume in itself. It is suggested that

the reader whose interest extends beyond the refining processes covered in this chapter consult the files and index of the *U.S. Patent Gazette* for further information.

Three processes for the refining of crude cottonseed oil have been employed commercially and have obtained a relatively wide acceptance

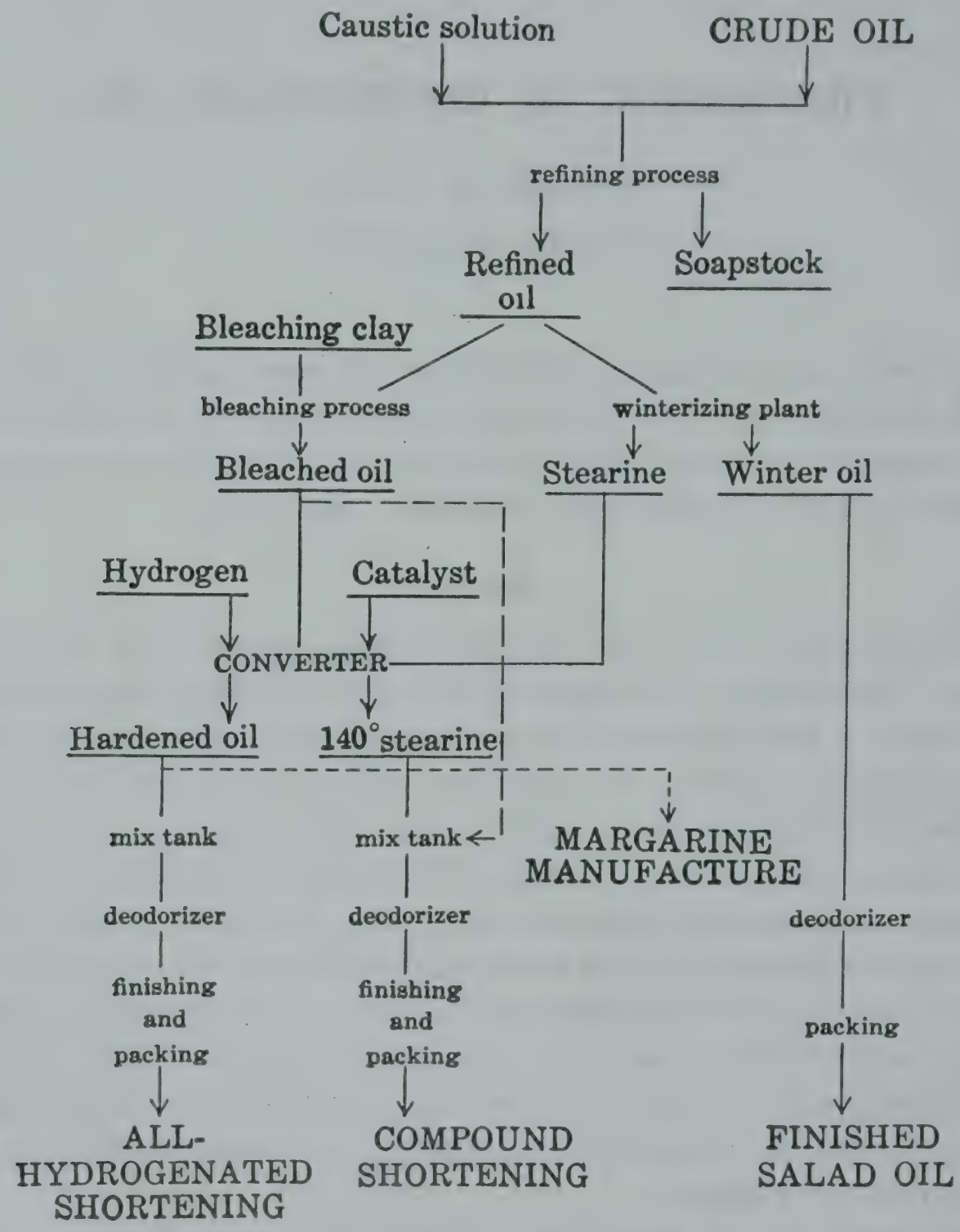


Fig. 178. Complete processing of cottonseed oil to produce edible products.

among manufacturers. The three processes are: (*a*) the open kettle method, now mainly obsolete but still employed in a number of small refineries and used occasionally in modern plants; (*b*) the continuous method of refining, which employs vigorous mixing of caustic and oil, and rapid heating followed by separation of the impurities from the refined oil by means of centrifugal separators [1]; and (*c*) a modified continuous method in two steps, the first of which employs soda ash solution to coagulate phospha-

[1] B. Clayton, W. B. Kerrick, and H. M. Stadt (to Refining, Inc.), U.S. Pats. 2,100,274 and 2,100,275 (1937).

tides and minor impurities and to neutralize free fatty acids, followed by separation of the coagulated material in a battery of continuous centrifugals.[2] Since soda ash does not remove the coloring matter from crude cottonseed oil as thoroughly as caustic soda solution, the neutralized oil from the primary separators is mixed continuously in the second step with caustic solution to remove more of the color bodies, and the mixture is heated and separated in another set of continuous centrifugal separators. The above three methods will be discussed in some detail.

A. Open Kettle Method

1. Design of the Kettle

Prior to the early 1930's, the open kettle was universally employed for the refining of cottonseed oil. Varying sizes and shapes of kettles were used, but that most generally accepted is a cylindrical tank equipped with a sweep agitator whose speed can be varied from a maximum of 30–35 r.p.m. to a minimum of 8–10 r.p.m. Such a kettle is approximately 10 feet in diameter and 14 feet deep to the top of the cone, the latter being pitched at an angle of 45°. A kettle of this size has the capacity of an ordinary 8,000-gallon (60,000-pound) tank car with sufficient outage in addition, to contain the required amount of caustic solution. The speed of the agitator is controlled by a standard variable-speed drive such as the Reeves or Llewellyn, and the agitator shaft is equipped with from 4 to 5 sweeps varying in length to avoid internal obstructions, such as skim pipes and coils. The sweeps are canted at an angle of approximately 45° and are constructed of steel plate about 4 feet long, 4 inches wide and ½ inch thick. They are arranged on the agitator shaft at intervals of about three feet and beginning at the top project radially at intervals of 90°. A bottom sweep which follows the cone is usually considerably shorter and wider than the others, in some cases resembling the blade of a plow.

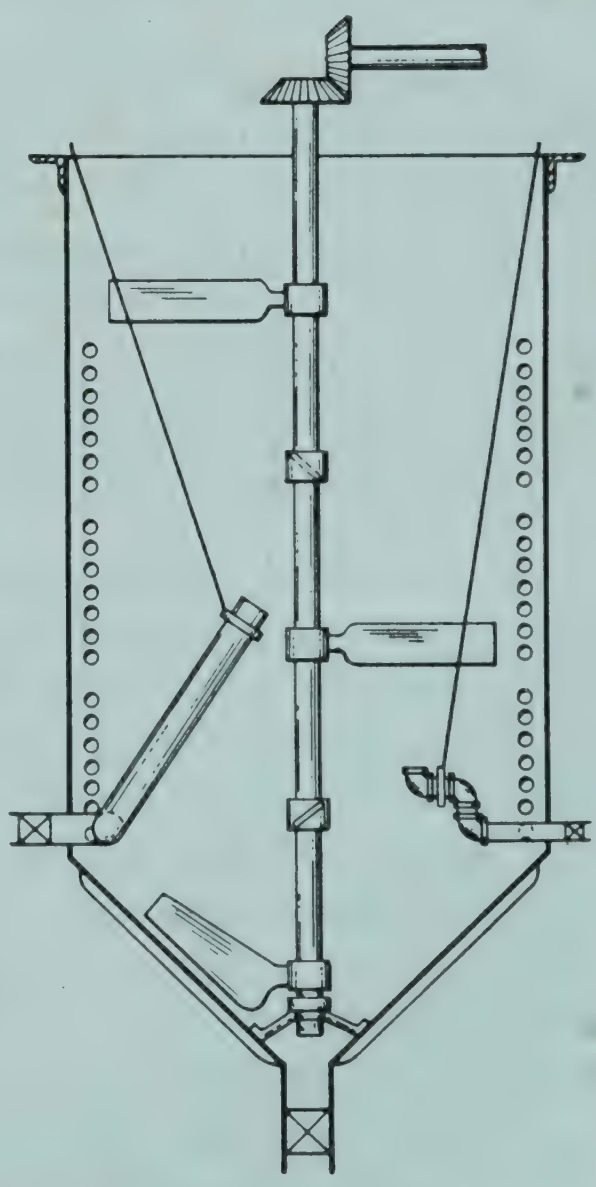


Fig. 179. Typical refining kettle.

The kettle is supplied with steam coils arranged in two or three indi-

[2] B. Clayton (to Refining, Inc.), U.S. Pats. 2,190,593 and 2,190,594 (1940).

vidual banks which empty into a common trap. Steam pressures normally employed range from 125 to 150 pounds gage. The cone of the kettle is provided with a stay-bolted steam jacket to which exhaust steam at 10 to 15 pounds pressure can be admitted.

The kettle is emptied with a draw-off or swinging suction pipe approximately 4 inches in diameter through which the oil can be pumped from above the soapstock, and in addition, a smaller swing line (2 inches) is provided for skimming the last few inches of oil from the surface of the soap. Soapstock can be withdrawn from the kettle through a 6- or 8-inch valve at the apex of the cone.

Figure 179 will serve to illustrate a typical refining kettle. The three banks of heating coils are merely indicated and the oil draw-off and skim line are in the draw-off position. When the agitator is running, they are pulled out of the way and the cables are stretched to clear the paddles.

2. Preliminary Laboratory Tests

As has been discussed in Chapter X, crude cottonseed oil is sold primarily on the basis of refining loss and color of the refined oil. These characteristics are determined by refining a small sample of the crude in the laboratory by the standard method laid down by the American Oil Chemists' Society, and the National Cottonseed Products Association. The results of the laboratory tests which have been carried out for settlement purposes are of great value to the refiner in determining the strength and percentage of caustic soda solution to be used in refining each individual tank car of oil.

The standard refining test is designed to indicate the lowest loss to be expected in kettle refining to give a color in the refined oil equal to or better than the prime color of 35 yellow, 7.6 red on the Lovibond scale. It is common practice to subject each sample of refined oil produced by laboratory refining to the official bleaching test of the American Oil Chemists' Society to determine the bleachability of the oil under consideration.

This official test consists of heating a sample of the refined oil to 120° C. under agitation at 250 r.p.m. and adding 6% (by weight) of official English fuller's earth. Agitation is continued for 5 minutes, not allowing the temperature to drop below 110° C., and the bleached oil is then filtered through paper.

Thus, from the combined standard refining and bleaching tests, the refiner can determine the yield to be expected and the bleachability of the refined oil on the tank car which is to be refined.

3. Selection of the Lye

In selecting the lye to be used in the kettle, consideration is given to the further processing steps to which the refined oil will be subjected. If it

is to be made into a shortening requiring a light color, sufficient caustic should be added in the kettle to give a minimum color on bleaching. On the other hand, if the refined oil is destined to be used as a yellow salad oil, it may be possible to reduce the amount of caustic solution and to obtain a slightly higher yield of dark refined oil.

To calculate the amount of caustic required in the kettle, the refiner determines the amount of dry sodium hydroxide needed to neutralize the free fatty acids in the oil, and to this amount he adds a certain excess for the coagulation of lipides and minor constituents. Generally speaking, for any given free fatty acid content, the excess required to give a good refining will vary directly as the loss obtained in the standard refining operation. Thus a crude oil having a free fatty acid content of 1% and showing a loss on standard refining of 5% will require less excess caustic than an oil of the same free fatty acid content which has a loss in the standard test of 9%, since the former contains a much smaller amount of lipides, etc., than the latter.

For normal refining to produce a bleachable oil, the excess of caustic above the theoretical will usually run from 0.20 to 0.35% (in terms of dry sodium hydroxide) for oils having free fatty acids of 2% or under. For oils with fatty acid contents above this range, the required excesses will be higher and in certain cases may be as much as 1.0%.

Having determined the percentage of dry sodium hydroxide required for the tank car under consideration, the refiner converts this figure to an equivalent percentage of caustic soda solution of from 14° to 18° Bé.

4. Refining Procedure

The net weight of crude oil contained in the kettle is best determined by pumping the oil from the tank car through a scale tank. When the kettle is charged, the agitator is started at medium speed and the temperature of the crude oil adjusted to 75–80° F. The speed of the agitator is then increased to approximately the maximum, and the lye, which is made up in a scale tank located above the kettle, is then run in as rapidly as possible, usually through a spray trough or a series of nozzle-type spreaders. Agitation at high speed is continued for 15 to 20 minutes to permit the greatest possible dispersion of caustic solution in the oil.

During this period, which is termed "agitation in the cold," the surface of the mixture of oil and caustic solution gradually assumes a slightly granular texture due to the agglomeration of particles of soap. This phenomenon is described as the "pin break." Its appearance is a signal for the refiner to slow down the speed of agitation slightly and to apply heat in the steam coils and the jacket. Under normal conditions, the temperature of the oil and soap in the kettle should be increased at a rate of approximately 2° F. per minute. As the temperature rises, the appearance of

the kettle changes, the "pin break" being replaced by a true break, due to the continued agglomeration of soft soap particles into larger and larger flakes. As the break progresses, the agitation should be slowed down progressively. The temperature of the oil should not be allowed to rise higher than 125–135° F.

As the size of the soap particles gradually increases, hand samples are withdrawn from the kettle and allowed to settle either in a glass container or a dipper. When the soapstock has become sufficiently soft to melt and run together in the hand sample, and when settling is rapid, the refiner judges the kettle to be finished.

Sometimes this finish occurs before steam is cut off from the coils and jacket; at other times it is necessary to run the kettle for some time with all steam off. Under these conditions, the speed of the agitator should be as low as possible. When the refiner judges that the foots settle sufficiently fast and coalesce to a sufficient degree in the bottom of the containers used for the hand sample, agitation is stopped and the mass is allowed to stand quietly for at least 8 hours. If time permits, a settling period of 14 hours is to be preferred.

After the kettle has been allowed to settle for the minimum time, the refined oil may be withdrawn through the larger of the swinging suction pipes into a scale tank. When the oil level reaches a point 3 to 4 inches above the surface of the foots, the large draw-off pipe is closed and the smaller or skimming line is opened. The last traces of oil are then skimmed from the surface of the foots. They may be added to the main body of oil withdrawn, but best practice requires that they be collected in a smaller scale tank as skimmings.

A skillful operator is able to skim the oil from the kettle with the inclusion of the minimum of foots. In many cases, the skim can be increased by running a portion of the foots off through the foots valve, thus contracting the surface of the residual oil and increasing its depth.

The gross yield of neutral oil from a refining is calculated by determining the difference between the weight of crude oil charged to the kettle and the weight of refined oil withdrawn.

Many refining kettles are equipped with foots tanks or pans immediately beneath the foots valve. These foots pans are often furnished with steam coils so that the foots may be heated and a further amount of oil withdrawn. Such recovered oil is usually dark in color and is not suitable for mixing with regular refined oil. It is normally added back to subsequent lots of crude oil to be refined.

Some refineries are equipped with washing kettles in which the refined oil can be washed with 5 or 10% of hot water to remove small quantities of soap held in the refined oil. The latter is sometimes dried in the same

vessel under vacuum and is sent forward either to immediate processing or storage.

When such equipment is not available, before storing refined oil it is customary either to filter it through a press loaded with spent cake from a previous bleaching operation or to treat it with a small amount (0.25%) of bleaching clay or infusorial earth before pumping to yard storage.

It is obvious from the foregoing that successful refining in the open kettle is dependent upon a high degree of skill and judgment on the part of the refiner. Crude oils from various sections of the country react differently and each season presents a new set of problems. The refiner's value to his employer depends to a large degree upon his experience, and this fact gave rise to a general superstition that the refining of oil was a mysterious art, rather than a manufacturing operation which might be made to conform to definite standards and be subject to reasonable routine control. The writer recalls a conversation some ten years ago with a refinery superintendent (who was also the chief refiner) who made the patently ridiculous statement that, due to his wide experience and vast knowledge of oil from the Southwest, he was able to smell a sample of freshly refined oil from the kettle and determine whether or not it was prime in color.

B. Continuous Caustic Soda Method

The first successful continuous refining process was developed in the early 1930's. This process employed centrifugals rather than gravity to separate soapstock from the refined oil. The time of contact between caustic and oil was also greatly reduced. Intimacy of mixing was attained by the use of either a small mechanical or a flow mixer into which continuously proportioned streams of crude oil and caustic were introduced.

1. Historical

The idea of continuous refining was not new. Martin Ekinberg,[3] in Europe, proposed a process for refining continuously through a battery of centrifugal emulsifiers and separators arranged in series, which was tried out commercially in 1893. Hapgood and Mayno [4] patented a process in 1923, for continuous refining which was extensively tested on a commercial scale, but which was never accepted.

The difficulty which prevented the successful adoption of the earlier continuous refining processes lay in the fact that no really satisfactory means for proportioning the oil and caustic were then available. This difficulty was finally surmounted by the development of the "propor-

[3] See L. E. Andes, *Vegetable Fats and Oils*, Scott Greenwood, London, 1897.
[4] C. H. Hapgood and G. F. Mayno (to DeLaval Separator Co.), U.S. Pat. 1,457,072 (1923).

tionometer." Essentially, the proportionometer consists of a positive displacement pump of the piston type which may be driven by steam, air, or hydraulic pressure (see Fig. 180). The length of stroke of the piston is adjustable so that varying amounts of caustic may be delivered. The

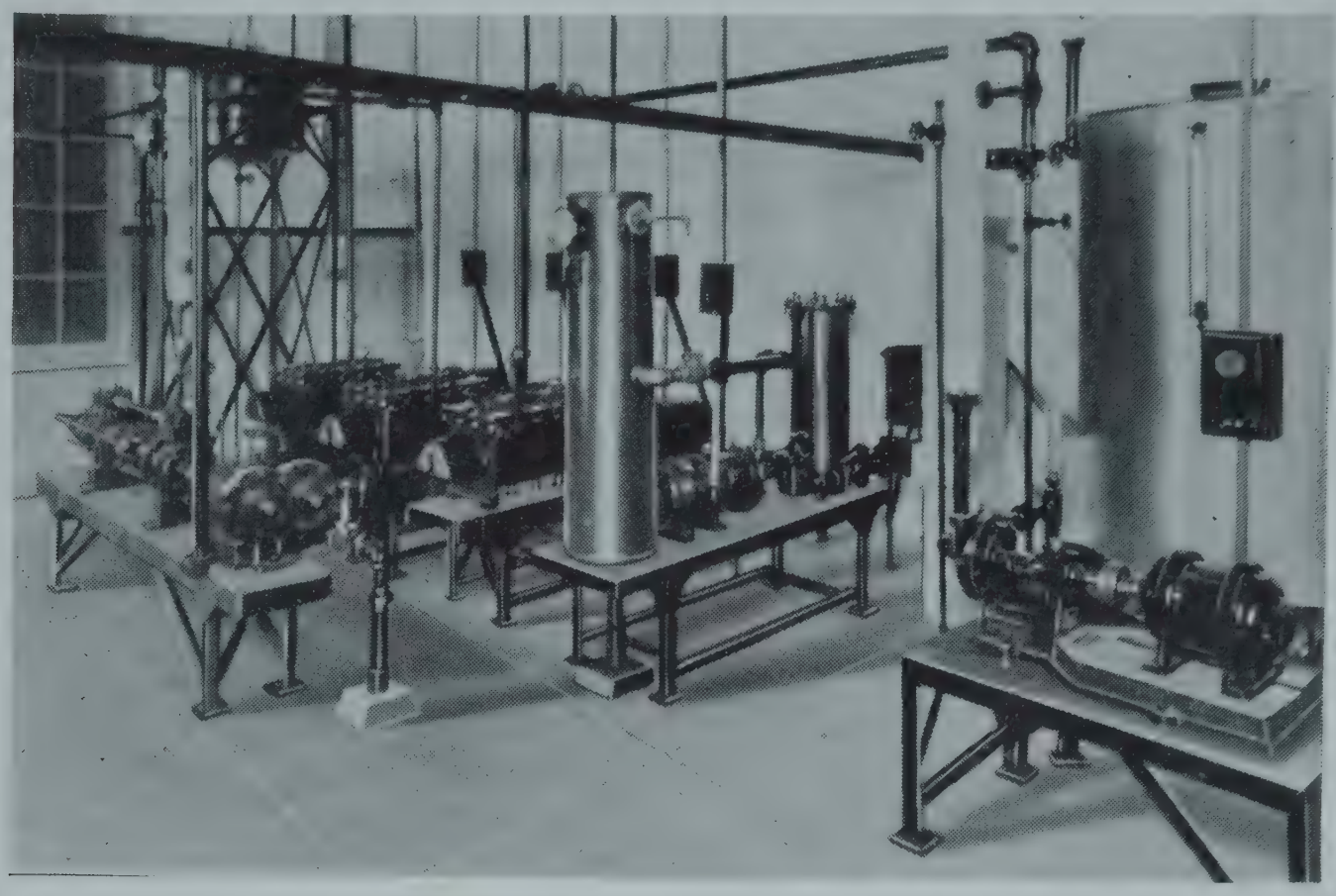


Fig. 180. Installation for the continuous refining of cottonseed oil, showing mixers and proportionometer. (Courtesy *The Sharples Corp.*)

pressure of the driving fluid is constant, and the valve of the pump is actuated by a positive displacement meter through which oil is pumped by either a centrifugal or gear pump. Thus, any slight increase in flow of oil through the meter will drive the meter pistons faster and step up the speed of the caustic pump. A decrease in oil flow will have the opposite effect. As a result, the ratio of oil to caustic delivered by the proportionometer at any time remains constant.

2. Apparatus and Method

A flow sheet of the regular continuous refining process is given in Figure 181.

Crude oil is pumped from a tank car or from storage into a crude feed tank, preferably mounted on scales. The temperature of the oil in the tank is adjusted to 75–85° F., the contents of the tank being agitated meanwhile to prevent settling of any small amount of meal which may be present in the oil.

Caustic soda solution of the requisite strength for refining, which may vary between 12° and 22° Bé., is made up in the caustic tank. The amount and strength of caustic desired is roughly determined by a study of the

standard laboratory refining results obtained on the oil to be treated. Generally speaking, the continuous method requires a somewhat larger excess of dry caustic to produce an oil of the required bleachability than is the case with the open kettle, since oil and caustic are in contact for a very short time in the former method. For the same reason, it is also possible to use lye of a somewhat greater specific gravity than is customary in the kettle.

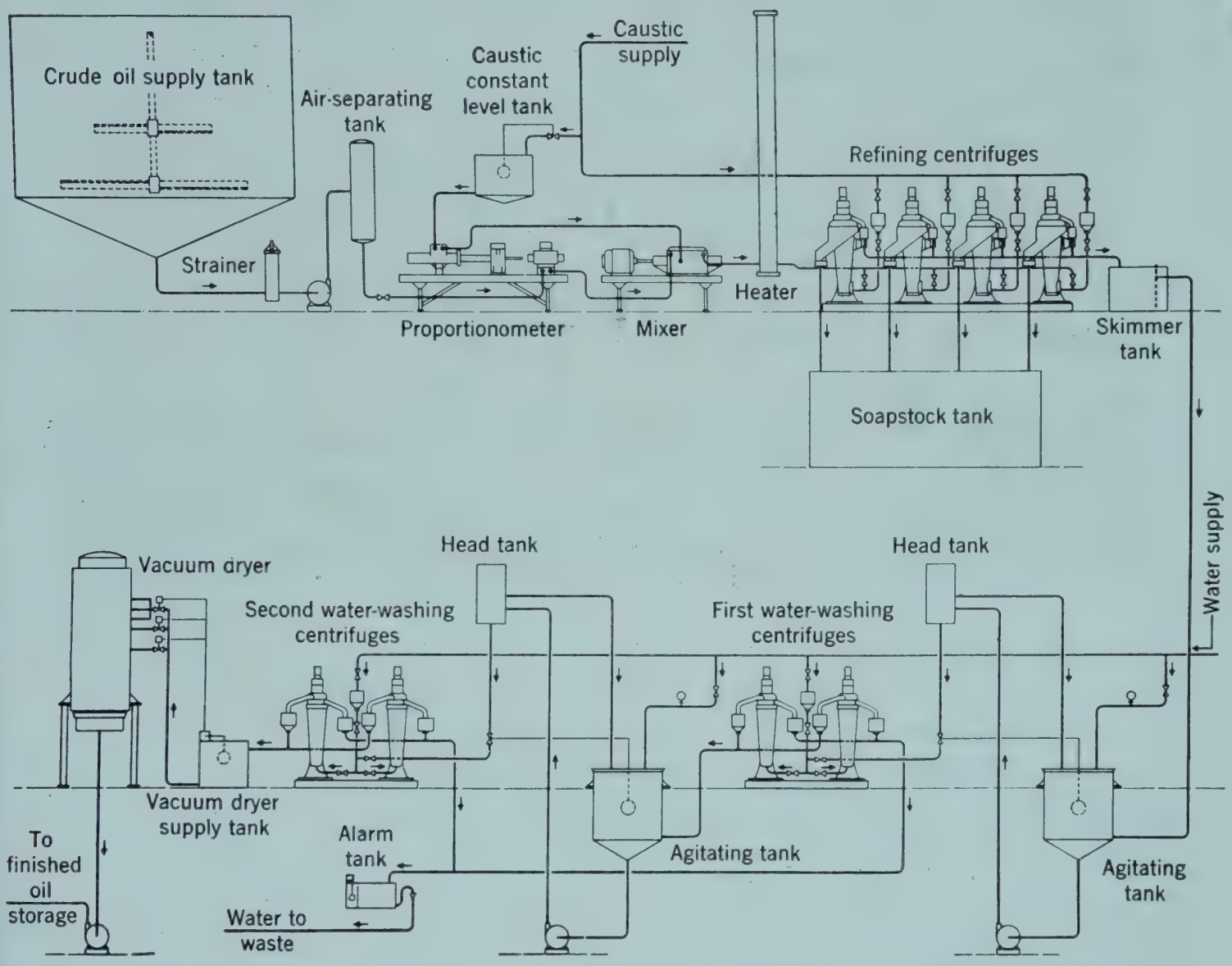


Fig. 181. Flow diagram of the continuous refining, double washing, and vacuum-drying of cottonseed oil. (Courtesy *The Sharples Corp.*)

Crude oil is pumped from the storage tank by means of the centrifugal pump through the meter end of the proportionometer. The flow actuates the valve mechanism on the caustic pump and a measured quantity of caustic enters the stream of crude. Oil and caustic meet in the mixer where they are intimately mixed for approximately one minute. The mixture then flows to a tube or coil heater, the heating medium being hot water or low-pressure steam. In the heater, the temperature of the mixture is raised to approximately 140° F. and a break takes place. From the heater, the refined oil, containing agglomerated particles of soapstock, flows to a battery of continuous centrifugal separators where the oil is discharged as a light effluent and the soapstock as a heavy effluent. The

total time during which oil and caustic remain in contact is approximately two minutes. The centrifugals are especially designed to allow the discharge of the soapstock as a plastic solid and it is dropped as directly as possible into soapstock storage.

The refined oil separated in the primary centrifugals contains a higher percentage of soap and moisture than is the case with well-settled oil which has been refined in the open kettle. Certain refineries give this primary oil no further treatment beyond a short settling in house tanks followed by a filtration, and thence pump it directly to storage. In this event, the gross yield is obtained by discharging the refined oil from the centrifuges to a scale tank and weighing.

3. Washing and Drying of the Oil

In the larger refineries, however, it has been found of considerable value to wash the oil from the primary centrifuges continuously with hot



Fig. 182. Installation for continuous refining of cottonseed oil, showing a double bank of primary centrifuges for separating oil and soapstock. (Courtesy *The Sharples Corp.*)

water in two stages, separating the soap water from the oil at each stage.[5] Usually, the first washing is carried out with 10% of hot water (180° F.)

[5] E. M. James (to Sharples Specialty Co.), U.S. Pat. 2,050,844 (1936).

added through a meter. The temperature of the oil in the wash tanks is kept at approximately 160° F.

The second washing is carried out with 5% of hot water at the same temperature.

Although the twice-washed oil is practically soap-free (20 p.p.m. or less), it still contains dissolved and suspended moisture. In order to make it suitable for storage, it is necessary to remove this moisture, which is conveniently accomplished through a continuous vacuum dryer [6] which reduces the moisture content to less than 0.10% (see Fig. 182). Oil with this much moisture will be clear and bright at room temperature.

From the continuous dryer, the oil is received in scale tanks and the yield is determined by the difference between the crude and refined oil weights. The storage of washed and vacuum-dried oil is much more simple than is that of oil which has been cleaned by filtration. Although anhydrous soap is practically insoluble in refined oil, wet soap is partially soluble. As a consequence, it is not practicable to remove all soap from refined oil by an ordinary filtration, and a small percentage finds its way to the yard storage tanks. The presence of this material in the refined oil will result in slight hydrolysis, particularly in the lower layers of the tanks and consequently an increase in the free fatty acid content. As a result, a foot or so of a large storage tank may consist of oil which is wet, and will contain free acids amounting to 0.2 to 0.3%. Such oil will require re-refining or washing with caustic before use. On the other hand, oil which has been continuously washed and vacuum-dried stores very well and tank bottoms are usually very small and present no problem in handling through the refinery.

4. Continuous vs. Kettle Refining

The yields obtained by the continuous refining process as compared with the open kettle process are in most instances materially higher. Generally, the higher the ratio of loss in the kettle to the free fatty acid content of the crude, the higher will be the net saving made by the continuous process. As a fair average, the net saving for prime crude oils by the continuous method will amount to 1.5 to 2.5% over the open kettle. It is possible to obtain larger savings when refining off oils that are high in free fatty acids.

The higher yields obtained by the continuous refining process are partially due to less saponification of neutral oil by the excess caustic and partially to less entrainment of neutral oil by the soap particles. The first reason is a direct result of the short time of contact between oil and caustic. The second is caused by the fact that, in the continuous method, centrifugal force (many thousand times the force of gravity) is employed

[6] A. U. Ayres (to Sharples Specialty Co.), U.S. Pat. 2,068,971 (1937).

to remove the foots from the oil, and it is unnecessary for the soap particles to be as large as in the open kettle. As a consequence, the total fatty acid content of the soapstock from the continuous process is much less than is that from open kettle refining.

Prior to the general introduction of the continuous refining process, soapstock containing less than 40% total fatty acids was not considered merchantable. Most of the soapstock from the continuous refining process would not meet this specification and it became necessary to reduce the permissible total fatty acids in soapstock offered for sale on the market to 35%.

While the principal advantage is the increase in the yield of refined oil to be expected, the continuous process is not nearly so dependent upon the judgment and experience of the refiner as is the case with the open kettle. Many variations which will adversely affect the results obtained with the latter are eliminated by the continuous process. If the refiner has misjudged the amount of caustic required to give an oil of the desired bleachability, it is a simple matter to increase the percentage by a slight adjustment of the proportionometer. If too much caustic is added, a cloudy oil from the primary machines or unusual fluidity of the foots will indicate this fact, and the caustic can be immediately reduced. Such changes during the refining process are impossible in kettle practice.

The adoption of the continuous refining process has been almost universal in the refineries in the United States and many foreign countries have also installed continuous plants.

C. Continuous Soda Ash–Caustic Soda Method

The third method of refining mentioned above was designed as an improvement on the original continuous method. Neutralization and decolorization are carried out in two distinct steps.[7] The process may be briefly described as follows.

A weighed lot, usually a tank car of 60,000 pounds, of crude cottonseed oil is pumped into the feed tank for the plant, and the temperature adjusted to the proper level. From the feed tank, the crude oil is picked up by a rotary or centrifugal pump and passed through a preheater and then to the meter end of the proportionometer, at a controlled rate. The reagent end is connected to a supply of soda ash solution of a strength between 15° and 20° Bé. and the piston stroke is adjusted to deliver 1.5 times the amount of solution required to neutralize the free fatty acids of the crude oil. The oil and carbonate solutions are mixed in a flow mixer and then passed through a coil where the mixture may be heated further. The soda ash solution neutralizes the free fatty acids of the oil to form soap, and at the same time coagulates the phosphatides or gums present in the crude.

[7] M. Mattikow, *Oil & Soap,* **19,** 83–87 (1942).

Since sodium carbonate will not saponify neutral oil, there is no loss from this source. The use of the large excess greatly reduces the formation of carbon dioxide because a considerable amount of sodium bicarbonate results from a reaction of the excess sodium carbonate and the free fatty acids.

From the heater, the mixture of partially refined oil, soap, and coagulated gums is introduced through spray nozzles into a "dehydrator," a tank maintained under 27–29 inches of vacuum by means of a conventional steam ejector. The tank contains an agitator to prevent settling of solids and steam coils to maintain the temperature. The water contained in the soap and coagulated gums is flashed off under the vacuum at the high temperature, and the solids are thus substantially dehydrated.

Dehydration under these conditions alters the character of the phosphatides and greatly reduces their solubility in the oil. At the same time, the tendency of the mixture of gum and soap to entrain oil is lessened. This change is not reversible and makes the subsequent step of rehydration possible.

From the dehydrating tank, the oil—at approximately 180° F.—is passed through another proportionometer where a further volume of 20° Bé. soda ash solution (from 2–7%) is added to rehydrate the phosphatides and soap. This rehydration is necessary to soften the dried soap and gums to allow them to discharge continuously from the centrifugals. The mixture is then passed through a battery of continuous centrifugal separators where the rehydrated gums and soap are removed from the deacidified oil. The latter is only partially decolorized. It is then passed through a cooler in which the temperature is reduced to 100° F. or slightly less, and is then continuously passed through a third proportioning device in which a 1–2% of 20° Bé. caustic soda solution is added. The oil and caustic are thoroughly mixed, and after passing through a coil heater, in which the temperature is raised to from 140° to 160° F., the mixture is separated in one or more centrifugal separators. The light effluent consists of thoroughly neutralized yellow oil, while the heavy effluent is a dark-colored, more or less viscous solution of soap and color bodies.

The refined oil from the second centrifuge is then continuously washed in two steps, as has been previously described, the soap water being separated in continuous centrifugal separators after each wash and the soap-free oil dried in a continuous vacuum dryer, from which it passes through a scale tank to storage. Yields are determined as before from the net weight of refined oil produced.

The two-step refining process in many cases will give a yield of 0.50 to 0.75% more refined oil than will conventional continuous refining. The bleachability of the refined oil is in all cases equal to, and in some cases slightly superior to, that obtained by regular continuous refining.

The use of the soda ash solution makes the process somewhat more costly than regular continuous refining, and more equipment is required to carry it out. The total fatty acid content of the soapstock or foots separated in the battery of primary centrifugals depends upon the amount of soda ash solution added for rehydration. Often it is sufficiently high to meet requirements of merchantable soapstock. However, in the case of



Fig. 183. Installation for continuous two-step refining of cottonseed oil, showing dehydrator in the foreground. To the right are centrifuges for separating the carbonate soapstock, the large centrifuge for separating caustic solution after the caustic treatment, and washing centrifuges. Vacuum dryer for the refined oil is in the background. Mixing and heating coils are shown on the left. (Courtesy *Refining Uninc.*)

crudes of low free fatty acid and relatively high phosphatide content, the soapstock must be acidulated with sulfuric acid to recover the fatty matter as acid oil. The large amount of sodium carbonate solution present increases the sulfuric acid usage and requires special precautions to avoid overflowing the tubs in which splitting is carried out.

To date, relatively few installations of the carbonate refining process have been made. However, the increased yields of refined oil make it appear attractive as a future development.

D. Storage of Refined Oil

The clean, dry, refined oil produced in the refinery is pumped to yard storage. A number of yard tanks should be available, since it is customary

to store refined oil of several grades, the grade of each depending upon the standard bleach test determined on a sample from the refined oil scale tank. Refined oil stores well, since when dry and soap-free, it is very stable. The bleach color, as measured by the standard bleach test of the American Oil Chemists' Society, remains constant over long periods of time. Cases are known in which the bleachability of refined cottonseed oil improves after several weeks' storage, and many refiners prefer not to continue the processing of freshly refined oil immediately, but pump it to storage to age.

E. Re-refining

In handling dark oils, it frequently happens that no matter how efficiently the original caustic refining of a crude cottonseed oil may have been carried out the bleachability of the yellow oil is less than desired for some purposes. Under these conditions, it becomes necessary to re-refine or wash the oil for color.

Such treatment can be carried out effectively in conventional continuous refining equipment or through the latter stages of a carbonate installation. One or two per cent of 16° Bé. lye is usually sufficient to produce a washed oil having a bleach color of from 2.0R to 2.5R on the Lovibond scale. In the case of a very dark refined oil which has been made from high-acid crude, more than one re-refining may be necessary. The loss resulting from such treatment through continuous refining equipment will range from 0.50 to 0.75% by weight.

Few refineries have sufficient continuous refining equipment to allow of both refining and re-refining, and it is usually necessary, at least during the refining season when crude receipts are heavy, to carry out the latter step in the open kettle. A common and generally satisfactory method of re-refining is performed as follows: The dark refined oil is pumped through the scale tank to a conventional open kettle. The agitator is started and the temperature adjusted to 75–80° F.

With the agitator running at full speed, 1.0 to 1.5% of 40° Bé. caustic soda solution is run into the oil and agitation in the cold is continued for 15 to 20 minutes. On account of the strength of the caustic solution and the consequent firmness of the soap particles formed, there is little tendency for the latter to coagulate. Steam is then turned into the coils and the agitation somewhat reduced. The temperature of the contents of the kettle is raised to 130–140° F. At this point, hot water (180–200° F.) is sprayed over the surface of the kettle and the agitator is slowed to considerably below medium speed. The hot water softens the tiny particles of hard soap, melts them, and causes them to agglomerate into relatively large flocs. Care must be taken not to add too much water, otherwise a cloudy oil and a very liquid soap will result. The judgment of the individual refiner at this point is of extreme importance. When sufficient water has been added to give

good melting and coagulation of the foots, the agitator is slowed to the lowest possible speed and run for 2 to 3 minutes. In the meantime, the refiner examines hand samples dipped from the kettle to determine the rate of settling and melting of the soapstock. When he judges the kettle to be finished, agitation is cut off and the batch is allowed to settle in the same manner as described for a regular crude refining.

Yields of re-refined oil by the above method will vary from 97.5 to 98.5% depending upon the skill of the refiner.

Generally speaking, the open kettle method of re-refining, due probably to the strength of the caustic solution employed, will give a re-refined oil having a somewhat lower bleach color than will continuous re-refining. Very strong caustic cannot be used in the continuous method, since the hard soap formed will not discharge from the centrifugal bowls, and the latter will rapidly clog and necessitate a shutdown for cleaning.

II. Bleaching

For the manufacture of shortening or of light-colored unhardened oils, the refined cottonseed oil must be further decolorized or bleached to remove the deep yellow color. This bleaching is accomplished by treating the oil at more or less elevated temperatures with small percentages of finely divided bleaching clays. Sometimes, activated carbon is used as an adjunct to the clay.

Bleaching clays fall into two categories: (*a*) natural clays, and (*b*) clays which have been activated by treatment with hydrochloric or sulfuric acid followed by removal of the acid by washing.

A. Equipment and Procedure

Most refineries carry out the bleaching operation in batches, either in an open bleach tank or in a vacuum bleacher.

The open bleach tanks commonly employed have a capacity of 15,000 to 50,000 pounds, and are equipped with steam coils and mechanical agitators. Usually, these bleach tanks are cylindrical, with a shallow cone bottom from which the mixture of oil and clay is pumped to the filter presses.

Vacuum bleachers are usually designed to treat 25,000 to 35,000 pounds of oil at a batch. They are also equipped with steam coils and mechanical agitators. A vacuum of 27 to 28 inches is maintained by means of a two-stage steam ejector.

It is customary to dry the refined oil under vacuum before adding the bleaching earth. In either case, the refined oil is heated to a temperature slightly in excess of 212° F. under strong agitation and 0.5 to 2.0% of bleaching clay is added. If activated carbon is employed, the amount is approximately 10% by weight of the clay. Generally speaking, the acti-

vated clays are more powerful bleaching agents than the natural clays and smaller amounts are required to give bleached oils with Lovibond colors equivalent to those obtained with natural clays.

After the addition of the bleaching earth, agitation is continued at the elevated temperature for 15 to 20 minutes. When bleaching is carried out in an open tank, the mixture of oil and clay is pumped through a recessed plate, or a plate and frame filter press, dressed with heavy canvas. The first effluent from the press is always slightly cloudy and the oil is, therefore, returned to the bleacher until it is adjudged clear. During recirculation, a bed of earth is built up on the filter cloths. When a clay-free effluent is obtained, it is transferred, usually by gravity, to house tanks for bleached oil.

With a vacuum bleacher, the same procedure is followed, except that before starting filtration the oil in the bleach tank is cooled to 160–180° F. by admitting cold water to the steam coils. The vacuum is then broken, and the oil and clay is pumped through the filter presses.

When a filter press has been filled with clay, the residual oil is recovered from the press by blowing first with air and then with steam. In certain cases, instead of using steam, hot water may be pumped through the press. The oil thus recovered is likely to be dark in color and is usually absorbed in refinery accumulations and re-refined rather than being sent directly for processing.

B. Losses in Bleaching

Losses in the bleaching operation have been the subject of much controversy. The same is true concerning the oil retained in the blown and steamed filter cake. Generally, activated clays will retain more oil than will natural clays. Activated carbons will retain more oil, on a percentage basis, than will either activated or natural bleaching earths.

If earth alone is considered rather than a mixture of earth and carbon, a natural clay will retain approximately 33% (on a dry basis) of its weight of oil. Thus, for every pound of clay added to the bleacher, 0.33 pound of oil will be retained in the spent cake.

An activated clay will retain approximately 50% of its weight of oil on a dry basis. Thus, one pound will retain 0.50 pound of oil. The activated carbons retain from 80 to 100% (on a dry basis) of their weight of oil.

The major cost of the bleaching operation, of course, will depend upon the original cost of the materials used in bleaching and the amount of oil retained in the spent cake. When oil—bleaching readily to light colors—is available, natural clays are very widely used, since their price is considerably lower than activated clays. Conversely, when the oil is difficult to bleach, the usage of activated clays rises. A further point to be considered is the price level of refined oil. When this is low, it is cheaper

to use somewhat larger percentages of the cheap natural clays than the more expensive activated clays, since the monetary value of the oil lost in the press cake is low.

The press cake, after blowing or washing, is usually sent to the dump. Since it contains a considerable amount of oil, it should not be allowed to accumulate in the refinery on account of the danger of oxidation and spontaneous combustion.

C. Recovery of Oil from the Adsorbent

Various means of recovering oil from spent bleaching earth have been attempted with varying degrees of success. In laboratory tests, it has been found possible, by immediate extraction of spent clay with light hydrocarbons, to recover an oil almost equal in color to the bleached batch. However, to attain such a result, it would be necessary to avoid any contact of the spent earth with air or steam, and such conditions are not practicable on a large scale.

Other organic solvents, such as benzol, acetone, or ether, will remove the coloring matter which the bleaching clay has adsorbed from the oil as well as the entrained glycerides and will always give a very dark product.

Several solvent extraction plants for the recovery of oil from spent cake have been installed and operated satisfactorily. The recovered stock, however, is so dark that it must be disposed of either as foots or added in small amounts to crude oil for re-refining. The profitable operation of a recovery plant depends upon the price of oil and other economic considerations.

Another method for recovering some oil from spent earth consists in boiling the press cake vigorously with a solution of soda ash and salt. Dilution of the slurry with water and allowing the whole to settle will cause a dark-colored oil to rise to the surface, whence it can be skimmed off. Yields by this method are low, and the recovered oil is disposed of as soapstock.

D. Choice of Adsorbents

Activated carbon alone has comparatively little bleaching effect on cottonseed oil, but when combined in small amounts with either natural or activated clays, it will give an oil of slightly better color than can be obtained with clay alone. Under certain conditions, the use of a small amount of carbon in conjunction with bleaching earth will also tend to improve the color stability of bleached cottonseed oil.

Natural clays, when used to bleach a clean, soap-free, refined oil, will give a bleached oil having the same or a slightly lower free fatty acid content than the original refined oil. On the other hand, activated clays will tend to raise the fatty acid content of the bleached oils slightly, and

this phenomenon may become serious when it is necessary to use relatively large amounts of activated earth in order to obtain satisfactory bleached oil colors. The increase in acidity of bleached oil caused by activated clay is more marked when bleaching is carried out in open tanks than when vacuum bleachers are employed. Activated clays also tend to cause press cloths to rot, due, in all probability, to their containing a small residue of mineral acid, and care must be exercised not to steam or wash the cake in the press for too long a time, in order to reduce this effect.

E. Batch vs. Continuous Bleaching

A considerable amount of experimental work has been done with continuous bleaching, and one or two installations of continuous equipment have been made. It is said that continuous mixing of earth and refined oil will appreciably reduce the percentage of clay required to obtain a given bleach color. In this author's experience, this has been true when the results of continuous vacuum bleaching are compared with those obtained in open bleach tanks. However, such is not necessarily the case when vacuum bleachers are considered, since in general, equipment of this type is appreciably more effective in producing light-colored bleached oil than is the open tank.

Following the refining and bleaching operations, the oil is ready for processing to finished products, and at this point the processing steps diverge, depending upon the ultimate product desired.

III. Winterization

If the oil is designed for consumption as salad oil, it must be winterized, that is, a considerable portion of the more saturated glycerides must be removed so that the material will remain bright under reduced temperatures, such as those likely to be encountered in the domestic icebox. Without the removal of the saturated glycerides, refined cottonseed oil will solidify at temperatures not much below 32° F.

A. Selection of Oil for Winterization

The percentage of removable glycerides or "stearine" may be estimated in advance from the iodine value of the oil. Refined oils made from crudes produced in the Mississippi Valley and the Southeast contain from 14 to 18% removable stearine, while those from Texas and Oklahoma may contain as high as 28%. Since the loss of such high percentages of stearine seriously affects the yield of processed salad oil obtained, it is customary for refiners producing both winter oil and shortening to subject the unwinterized oil to a preliminary topping in yard storage tanks. When a yard tank has been filled, it is allowed to settle at outdoor temperatures. During the fall and early winter when temperatures are not too low, this

results in a crystallization and settling out of the more saturated glycerides or stearine. Oil for the winter oil plant is withdrawn from the upper layers of the storage tank, while oil destined for shortening manufacture is withdrawn from the lower layers. This procedure results in the double benefit of higher oil yields from the winter oil plant, and less required drop in iodine value in converters in the hydrogenation plant.

B. Winterization Procedure

Oil to be winterized must be clean and dry and it is customary to give it a light cleaning bleach. The winterizing tanks, contained in a well-insulated room equipped with refrigeration, are then filled with dry oil at a temperature between 90° and 95° F. Some plants are equipped with brine coils in the winterizing tanks, while others make use of brine and ammonia coils to chill the entire room. Temperatures are so adjusted that a charge of oil of approximately 40,000 pounds will drop to 38–40° F. at a uniform rate in about three days. A careful chart of the drop in temperature per hour is kept for each tank and, as the end of the chilling period approaches, the temperature is watched very closely. As the more saturated glycerides crystallize from the oil, the release of the latent heat causes the temperature of the whole mass to rise 2° or 3° F.

When this heat has been absorbed, the temperature begins to fall again. The proper time to start filtration is determined as that point where the temperature of the tank begins to fall below the lowest temperature attained immediately preceding the afore-mentioned rise.

Recessed plate, or plate and frame filter presses, dressed with heavy canvas, are used for the separation of the oil and stearine. These presses should be contained in a refrigerated room maintained at a temperature of 36–38° F. The mixture of oil and stearine may be forced to the presses, either by transferring from the chilling tank to a closed drum which is maintained under 15–20 pounds air pressure, or by removal from the chilling tank by a gear pump set at a constant pressure which is controlled by a relief valve and by-pass.

The pressure on the presses is maintained at a constant value and the press is known to be full when oil ceases to flow from the press cocks. Free oil retained in a full press is removed by blowing with cold air.

When the press is cleaned, the stearine is removed by separating the leaves and scraping the press cloths with hand scrapers. It is allowed to drop into a hopper below each press; the hoppers are equipped with small steam coils so that the stearine can be melted and pumped away.

C. Specifications. Yields

The trade specifications for winterized cottonseed oil require that the oil pass the standard cold test of the National Cottonseed Products Asso-

ciation. In this test, a four-ounce bottle is filled with the winterized oil and is tightly corked—the cork is sealed with paraffin. The sample bottle is then immersed in cracked ice, enough cold water being added to rise through the ice to the top of the bottle. Fresh ice is added from time to time to keep the container solidly filled. The oil should remain clear and bright at this temperature for at least 5½ hours.

By sending only topped oil to the winter oil plant, it is sometimes possible to obtain yields of winter oil in excess of 90%, as compared with yields of 75–84% when untopped oil is used.

The winter oil stearine is usually consumed in compound shortenings or is fully hardened for flake stearine. The winterized oil which has passed the standard cold test is now ready for deodorization.

IV. Hydrogenation

Cottonseed oil is widely employed in the manufacture of shortenings for commercial and household use. For this purpose it is necessary to change it from a liquid at room temperature to a plastic solid. How this process is carried out will depend whether an all-hydrogenated or a compound-type shortening is being manufactured.

Manufacture of the former depends upon hardening the entire mass of oil to a given consistency, while that of the latter consists of hardening a part of the oil almost completely to 140° stearine, and blending this with unhardened oil to obtain the desired degree of plasticity. A measure of consistency frequently used is the iodine value–congeal point relationship. The congeal point of a fat is defined as the highest temperature attained in the cooling curve of the melted fat determined under fixed conditions.

Much has been written upon the subject of the hydrogenation of vegetable oils. Perhaps the best known work upon this subject is the volume by the late Carleton Ellis.[8] A complete discussion of the mechanics of the reaction between hydrogen and the glycerides of unsaturated fatty acids or a consideration of the numerous courses that the reaction may take are beyond the scope of this chapter. However, the following paragraphs will serve to outline briefly modern practices in the commercial hydrogenation of cottonseed oil.

A. General Characteristics of the Reaction

Hydrogenation is ordinarily accomplished by the treatment of cottonseed oil with hydrogen under moderate pressure, in the presence of a catalyst—usually finely divided nickel—supported on infusorial earth and suspended in the oil.

The type of catalyst employed controls the characteristics of the final

[8] C. Ellis, *Hydrogenation of Organic Substances,* 3d ed., Van Nostrand, New York, 1930.

product to a great extent. Some catalysts are extremely active, that is, they promote exceedingly rapid absorption of hydrogen, but are relatively nonselective; while others may be more selective, but much less active.

The term "selective" as used here refers to the iodine value–congeal point relationship in the hydrogenated oil rather than specifically to the reaction of linoleic in preference to oleic acid. This relationship may be affected both by the order in which the unsaturated acids absorb the hydrogen and the formation of iso-oleic acid, a high-melting isomer of normal oleic acid.

A typical unhardened cottonseed oil contains in its glycerides approximately 1% stearic and 23% palmitic acids. The unsaturated acids are approximately 49% linoleic and 27% oleic. During hydrogenation, neither the original stearic nor the palmitic acid is changed. If the hardening follows the theoretical course of selective hydrogenation before any hydrogen is absorbed by the oleic acid, the linoleic acid will be converted to oleic. On the disappearance of the linoleic acid, the oleic acid will next absorb the hydrogen, and if the hydrogenation is allowed to proceed to completion, the oleic will finally be converted to fully saturated stearic acid. Such a theoretical reaction is never attained in practice. How closely it is approximated will depend principally upon the catalyst.

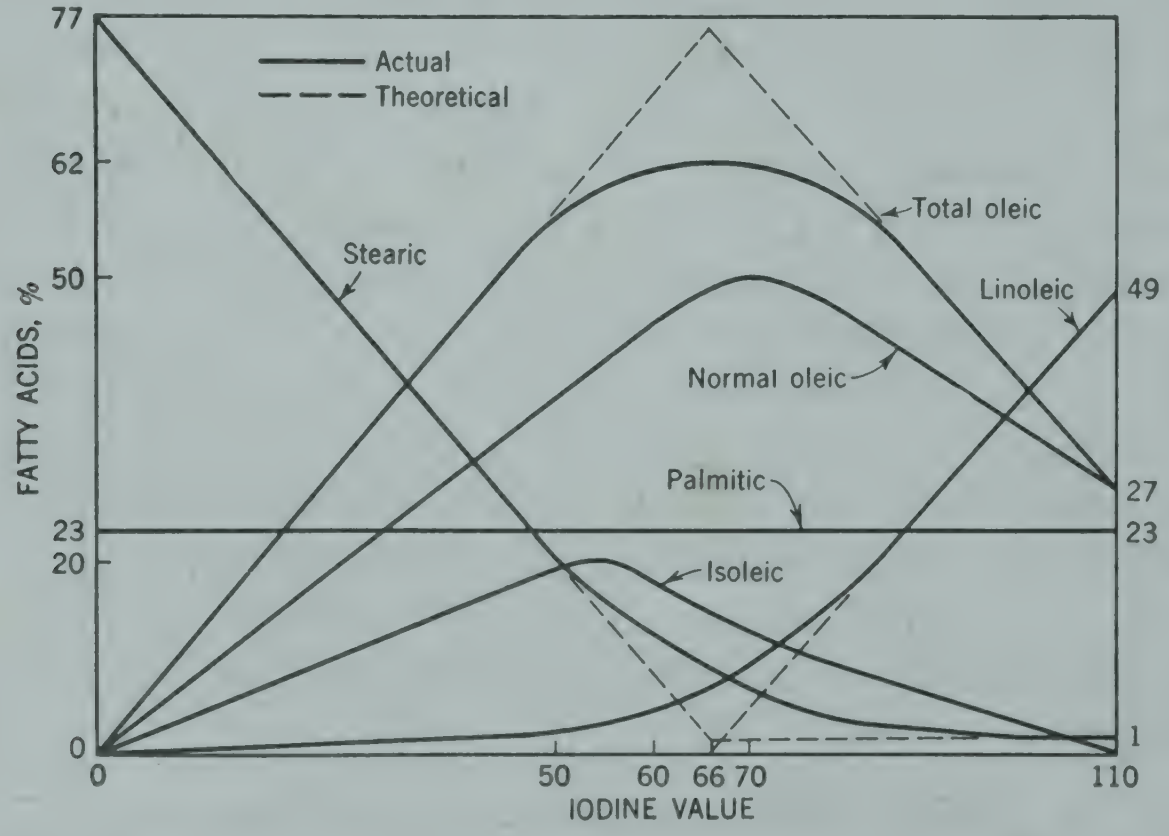


Fig. 184. Composition of selectively hydrogenated cottonseed oil.

Figure 184 shows the course of hydrogenation of cottonseed oil of 110 iodine value with a good selective catalyst. It will be observed that as the iodine value drops, although the total amount of normal oleic acid is increased markedly, this increase is accompanied by the appearance of iso-oleic acid. The glycerides of this acid are solid at room temperature.

A nonselective catalyst, in addition to leaving considerable amounts of unaffected linoleic acid, will tend to increase the percentage of iso-oleic glycerides formed by the hydrogenation of the linoleic acid glycerides. The congeal point will then be dependent upon the amount of stearic acid glycerides and iso-oleic acid. The resultant product at any given iodine value will have a noticeably higher melting point than would be the case had the hydrogenation proceeded more selectively to form oleic glycerides with a minimum of the high-melting products.

It has been found that the temperature at which hydrogenation is carried out also has an effect on the selectivity. Generally, hardening is more selective at relatively low temperatures than at higher temperatures. However, the reaction proceeds so much more slowly at low temperatures as to be impracticable commercially beyond certain limits. Working temperatures which are generally used range from 150° to 200° C.

Since keeping quality or resistance to oxidative rancidity is directly associated with the iodine value, it follows that a hydrogenated fat containing high percentages of iso-oleic acid glycerides with unhydrogenated linoleic acid will be less stable than a similar fat of the same melting point containing lower percentages of these same glycerides.

A selectively hardened stock will melt slowly and remain plastic for some time. On the other hand, a nonselectively hardened stock containing high percentages of iso-oleic acid will show a sharper melting point. This property is advantageous when the hardened stock is destined for use as a component in margarine, since the sharp melting point at body temperature gives a more pleasant sensation in the mouth than does a gradual melting. The former property is a characteristic of butterfat.

B. Catalyst

From the foregoing, the important role played by the catalyst in hydrogenation is obvious. Some refiners prefer to manufacture their own catalyst, while others purchase it on the open market from specialists in this field. It is not our purpose to enter into a discussion of the various types of catalyst available. Ellis [8] covers this point exhaustively and the reader is referred to his book. Some of the more selective catalysts are extremely susceptible to catalyst poisons and will lose their activity very rapidly unless pure hydrogen is used. Such catalysts cannot be re-used frequently. Others, which are not so selective, are resistant to catalyst poisons and may be used several times without much effect on their activity and such selectivity as they may possess.

The catalyst is usually prepared from nickel carbonate or hydroxide by reduction to metallic nickel, at high temperature, in an atmosphere of hydrogen. At the conclusion of the reduction, the catalyst is suspended in oil in order to protect it from oxidation and also as a convenience in

handling. The catalyst is sometimes prepared from an organic salt of nickel, such as the formate, by suspending it in coconut oil or other oil and reducing it to metallic nickel with hydrogen. This is a convenient method which requires comparatively simple equipment.

C. Hydrogen Production

The hydrogen gas used for hardening cottonseed oil should be as pure as practicable so as not to "poison" or inactivate the catalyst. Some manufacturers have found it advisable either to manufacture or to purchase electrolytic hydrogen, which has a high degree of purity. The cost of electrolytic hydrogen is high unless power is very cheap. A large proportion of the hydrogen used today is made by the steam-iron process. The steam-iron process depends upon the alternate oxidation and reduction of iron ore when treated with water gas and steam at temperatures between 550° and 800° C. Water gas, or blue gas, is prepared by the treatment of coke with water vapor at elevated temperatures according to the following reactions:

$$C + 2\,H_2O \rightarrow 2\,H_2 + CO_2$$
$$C + CO_2 \rightarrow 2\,CO$$

Water gas from the blue gas generator contains approximately 38% carbon monoxide and 49% hydrogen; the balance is carbon dioxide and nitrogen.

The alternate oxidation and reduction of the iron in the hydrogen generators by steam and water gas are summarized by Taylor [9] as follows:

Oxidation

$$3\,Fe + 3\,H_2O \rightarrow 3\,FeO + 3\,H_2$$
$$3\,FeO + H_2O \rightarrow Fe_3O_4 + H_2$$

Reduction

$$Fe_3O_4 + H_2 \rightarrow 3\,FeO + H_2O$$
$$3\,FeO + 3\,H_2 \rightarrow 3\,Fe + 3\,H_2O, \text{ and}$$
$$Fe_3O_4 + CO \rightarrow 3\,FeO + CO_2$$
$$3\,FeO + 3\,CO \rightarrow 3\,Fe + 3\,CO_2$$

Steam-iron gas contains small amounts of a number of impurities, in addition to carbon dioxide, the most important of which are carbon monoxide and hydrogen sulfide derived from the blue gas. Carbon dioxide is removed by scrubbing with caustic soda solution.

The hydrogen sulfide, which will poison the catalyst, is removed by passing the scrubbed hydrogen through sawdust and shavings coated with hydrated ferric oxide. In addition to the carbon dioxide and hydrogen sulfide from the generators, there is a small amount of carbon monoxide present. Various means for removing the latter by catalytic agents have been developed. The Harger-Terry method,[9] which removes carbon mon-

[9] H. S. Taylor, *Industrial Hydrogen*, Chemical Cat. Co., New York, 1921.

oxide by preferential oxidation to carbon dioxide at 200–300° C. over a mixture of iron, chromium, and cerium oxides as a catalyst, is a good example of such a purification process. It is possible to remove 95% of the carbon monoxide from steam-iron hydrogen with an initial carbon monoxide content of 0.4–0.5%.

A third source of hydrogen is a process recently put on the market which depends upon the treatment of a mixture of light, normally gaseous hydrocarbons (such as propane or butane) and steam, with a metallic oxide as a catalyst at temperatures of the order of 1,500° F. Hydrogen is liberated from the hydrocarbons and the steam; and carbon monoxide and carbon dioxide are formed from the carbon atoms.

The gases are cooled with additional steam to about 700° F. and passed over another catalyst where the bulk of the carbon monoxide is converted to carbon dioxide, which is removed by scrubbing the gases with monoethanolamine solution. The mixture of hydrogen and the remaining carbon monoxide is then heated and passed over a second bed of conversion catalyst where again the bulk of the remaining carbon monoxide is converted to carbon dioxide and then scrubbed out. The carbon monoxide conversion and scrubbing operation is repeated a third time in order to reduce the carbon monoxide content of the finished gas to a concentration low enough to make the gas acceptable for oil hydrogenation. As an alternative, the third conversion and scrubbing operation may be replaced by a methanation process wherein the remaining traces of carbon monoxide are reduced to methane. The reactions involved are typically as follows:

$$C_3H_8 + 4\,H_2O \rightarrow 2\,CO + CO_2 + 8\,H_2$$
$$2\,CO + 2\,H_2O \rightarrow 2\,CO_2 + 2\,H_2$$

Methanation $$CO + 3\,H_2 \rightarrow CH_4 + H_2O$$

This process or modifications of it have been widely used in the petroleum industry, and recently several installations have been made for the manufacture of hydrogen for the treatment of vegetable oils.

D. Hydrogenation Practice

1. Batch Hydrogenation

Hydrogenation is carried out in a vessel known as a converter. The converter is a cylindrical tank, as shown in Figure 185, usually upright, and capable of withstanding pressures of up to 150 pounds gage. It should be well lagged and equipped with cooling and heating coils and suitable devices at the bottom for distributing the hydrogen through the oil. Converters are usually furnished with mechanical agitators. Hydrogen is

picked up from the gas holders by a compressor and the pressure in the converter is maintained in the desired range, which is ordinarily 10 to 50 pounds.

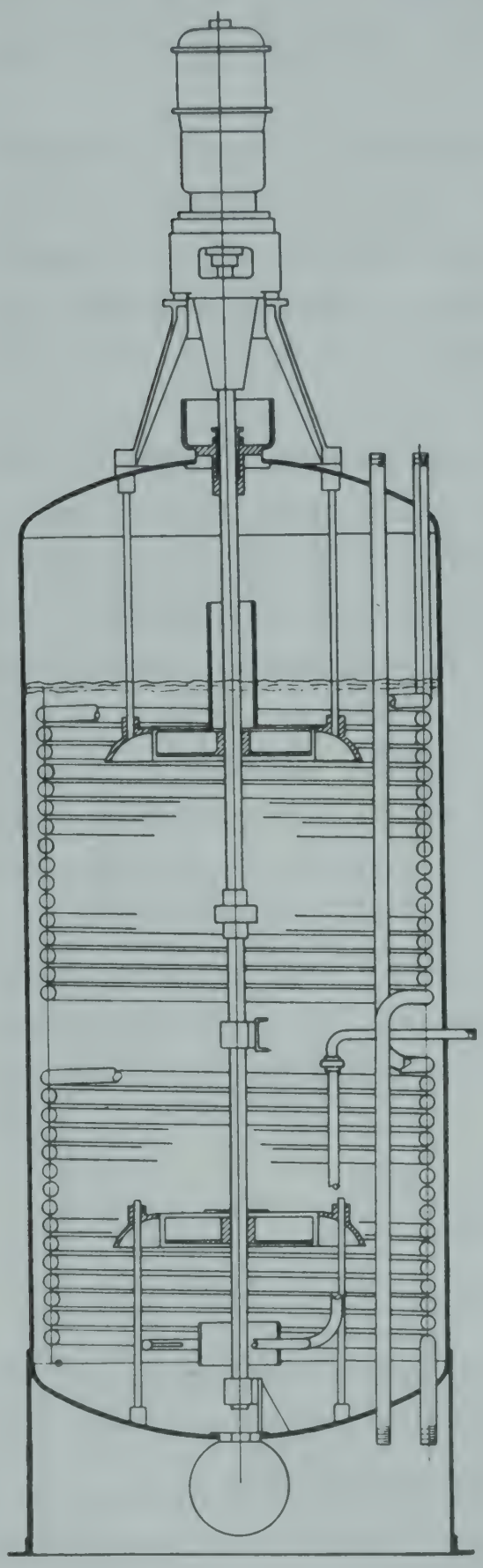


Fig. 185. Sketch of typical converter for hydrogenation, with mechanical agitator. (Courtesy *Sieck & Drucker, Inc.*)

Refined and bleached cottonseed oil, in which a small percentage of the reduced catalyst has been suspended, is pumped into the converter and the temperature is raised to 100–120° C. (under agitation), with a stream of hydrogen. At this temperature, absorption of hydrogen becomes rapid and, since the reaction is exothermic, the temperature rises rapidly. When the desired temperature is attained, it is controlled by admitting water to the cooling coils. The excess of hydrogen admitted to the converter over that which is absorbed collects above the surface of the oil.

Any carbon monoxide present in the hydrogen is not absorbed by the oil and hence tends to build up in the hydrogen as a diluent. When the percentage in the gas becomes appreciable, the absorption of hydrogen slows down. At this point, the usual practice is to purge the converter by allowing the gas above the oil to escape to the atmosphere. The frequency of purging is, of course, dependent upon the percentage of carbon monoxide in the original gas. The presence of sulfur compounds, which may have escaped the iron oxide shavings purifier, will also tend to slow down the hydrogenation by poisoning the catalyst, and may reduce its activity to nearly zero. In such a case, purging will not serve to correct the condition, and a fresh charge of catalyst must be introduced to the converter.

The progress of hydrogenation is usually followed by measuring the drop in refractive index of the oil in the converter. The relationship between iodine value and refractive index is very nearly a straight line function. When the desired reading is obtained, the flow of hydrogen is cut off and the charge in the converter is cooled to temperatures suitable for filtering out the catalyst.

Filtration is accomplished by pumping through standard recessed plate, or plate and frame filter presses, dressed with canvas. The clear oil is accumulated in house storage tanks for further processing. The catalyst remaining in the press may be steamed to remove residual oil if it is fully spent, or it may be reused to harden another bath of oil. Some catalysts can be reused a number of times, although both selectivity and activity tend to be reduced through reuse.

Fully hardened cottonseed oil or 140° stearine is produced from refined and bleached cottonseed oil or from stearine from the winter oil plant. The iodine value is reduced to 15 units or less.

During hydrogenation, the color of the oil tends to become lighter, and the free fatty acids tend to increase somewhat. In certain cases, the latter may be too high to be removed in the deodorizing process and it may become necessary to re-refine the hardened stock to bring it down to a satisfactory level. The re-refining is a source of loss which tends to raise the cost of the hardening operation, and can be avoided by controlling the free fatty acids of the refined and bleached oil.

Advantage is sometimes taken of the color drop in the converter by hardening a clean, filtered, refined oil rather than a bleached oil. In this case, the hardened oil is not light enough to meet the usual standards for finished shortening, and must be bleached strongly with fuller's earth after the nickel catalyst has been filtered out.

2. Continuous Hydrogenation

A continuous process for the hydrogenation of cottonseed oil has been available for some time, but has not been used commercially in this country. The process was known originally as the Bolton and Lush, and later as the T.R.W. Continuous Process.[10]

Hydrogenation is carried out in a number of drawn steel-jacketed tubes, arranged in series. Each tube is approximately 7 feet long and 6 inches in internal diameter. Each tube is fitted with two catalyst cages, each 3 feet 6 inches long and 6 inches in diameter. The cages are built of Monel metal gauze and are filled with nickel turnings whose surface has been activated. Oil to be hardened is contained in a tank, fitted with heating coils, sight and pressure gages, etc., which is connected to one end of the series of tubes. At the other end is a separator (to allow the escape of hydrogen from the finished oil) and a continuous cooling coil. The working pressure is 150 pounds gage. The largest plant offered is rated at a capacity of approximately 33,000 pounds of hardened cottonseed oil with a melting point of 40–42° C. per 24-hour day.

The catalyst cages are activated electrolytically by covering the metal with a thin film of nickel oxide. The cages are immersed in dilute sodium

[10] Technical Research Works, Ltd., *Hydrogenation of Oils and Fats,* London.

carbonate solution, and surrounded by a thin sheet of nickel, which forms the cathode, the cage itself being the anode. From 24 to 48 hours are required for the necessary oxidation. The cages are then washed and placed in the reaction tubes. The tubes are closed, superheated steam is turned into the jackets, and the oxide is reduced to active nickel by a stream of hydrogen.

Oil to be hardened is pumped into the feed tank, is preheated, and when the desired temperature attained, is forced by hydrogen pressure from the feed tank into the main supply line where it meets a current of hydrogen. Oil and hydrogen pass together into the top of the first tube, and the oil drips through the catalyst to the bottom, whence it is forced to the top of the second tube, and so on through the whole series, being at all times in contact with hydrogen.

At the end of the line, the oil is received in the separator, where it is freed from excess hydrogen, and is then cooled continuously in the cooling coil to a suitable temperature for discharge to the atmosphere. Filtration of the hardened oil is unnecessary, since the catalyst is not suspended in it.

When it becomes necessary to reactivate the catalyst cages, they are first freed from oil by washing with a suitable solvent, and the surface is again oxidized and then reduced as described above. Although the massive catalyst employed in the continuous process remains active for some time, it is not so selective as many of those employed in the standard batch procedure. This fact and the relatively small capacity of the plant have been two of the reasons militating against its adoption in the United States.

3. Characteristics of the Products

All-hydrogenated shortenings are usually hardened directly to approximately the iodine value and congeal point desired. Compound-type shortenings, it will be remembered, are prepared by blending 140° stearine with bleached, unhardened oil, the amount of the former added varying between 4 and 10%, depending upon the product desired. It is obvious that the stability of a compound shortening will be less than that of an all-hydrogenated product, since the former contains a considerable quantity of the more unsaturated glycerides which have been reduced in the latter.

Fully hardened cottonseed oil or 140° stearine, immediately after hardening, is often solidified into flakes on a brine chilled roll, and the flakes sacked for storage. Some refiners prefer to purchase flaked 140° stearine rather than manufacture it themselves. The flaked product keeps and ships well and will dissolve rapidly in the warmed bleached oil.

Winterized cottonseed oil has a characteristic taste and smell. Bleached oil has a slight earthy taste and odor; hydrogenated oils have a peculiar metallic taste and smell which have been described as the "hydrogena-

tion" characteristic. In order to produce the bland oils of commerce, winter oils and shortenings must be deodorized.

V. Deodorization

Deodorization is accomplished by subjecting the stock to the action of superheated steam at high temperatures under very low absolute pressures. Winter oil is usually deodorized at somewhat lower temperatures than compound or all-hydrogenated shortenings.

A. Nature of the Process—The Wesson System

The earliest of the successful high-temperature deodorization processes under vacuum was that devised by the late David Wesson. In the Wesson process, the oil being deodorized is circulated to and from the deodorizer through a series of tubes heated by direct firing. The deodorizer is a vertical tank maintained under low pressure and equipped with a steam spider through which superheated steam is admitted. The substances responsible for the characteristic odor of the stock are volatilized with the steam, which is condensed in a barometric condenser. (Sometimes the Wesson process was modified by the installation of several deodorizers in series, and the oil, instead of being circulated back to the same vessel, passed from one deodorizer to the next.) After exposure to the high temperature and steam for several hours, the oil is cooled to approximately 120° F. and then filtered to remove traces of dirt and foreign matter.

B. Deodorizer Design

The usual method of carrying out deodorization today is by treatment with superheated steam in tanks holding from 10,000 to 30,000 pounds of stock. The deodorizer is a hammer-welded vertical steel vessel, cylindrical in shape with a dish bottom and rounded top, and sufficiently tall to allow a large space to remain above the surface of the oil. This outage is necessary to avoid the danger of splash-over of the oil, since under the low pressures employed, agitation caused by the open steam is violent. The deodorizer or still is heavily lagged to minimize heat losses. The top of the deodorizer is equipped with baffles to avoid entrainment of oil in the steam. A large vapor pipe, 18–24 inches in diameter, is welded to the top of the deodorizer and leads to a catchall. The latter is a cylindrical baffled tank, supported above the deodorizer. From the catchall, a similar vapor pipe leads to the ejector system which may be a two-stage or a combination of a thermocompressor and a two-stage ejector. A large part of any entrained oil leaving the deodorizing vessel is caught in the catchall. The steam and volatile odoriferous materials, as well as traces of free fatty acids distilled off from the stock, are condensed in a barometric condenser

and hot well. A steam spider for the superheated steam, an oil draw-off, and charging lines are provided.

1. Heating and Cooling of the Charge

Heat is furnished by a series of coils in the deodorizer, the heating medium being heavy mineral oil, Dowtherm (a mixture of diphenyl oxide and diphenyl) vapor, or high-pressure steam. Circulating mineral oil is heated in direct-fired tubes and pumped through the heating coils. Dowtherm (which boils at 500° F. at atmospheric pressure) is vaporized in a conventional Dowtherm boiler, fired by fuel oil or gas, and is circulated through the coils at low pressure, condensed, and revaporized in the furnace. High-pressure steam requires a special boiler plant with the proper valves and lines.

Of the three methods of heating, Dowtherm heating is probably the most economical for the average plant when high-pressure steam is not available (see Fig. 186). Dowtherm is superior to mineral oil as a heat

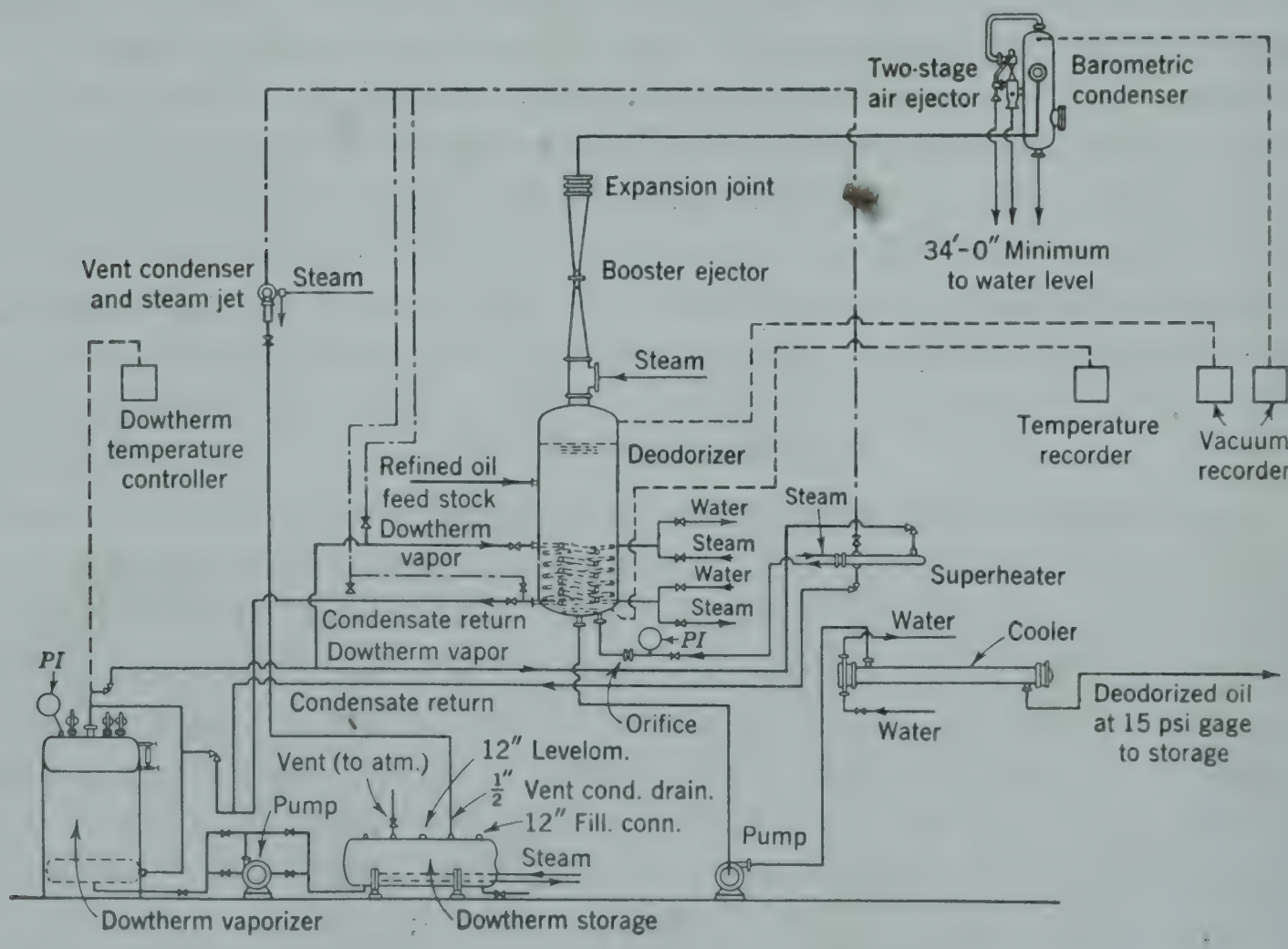


Fig. 186. Flow sheet of a modern batch deodorizer installation with Dowtherm heating. (Courtesy *Foster Wheeler Corp.*)

transfer medium on account of its stability. A small leak in the lines outside of the deodorizer can be easily detected from the characteristic geranium odor, and any traces getting into the oil will be carried off by the blowing steam. Mineral oil, on the other hand, tends to crack to some extent at the furnace temperatures, and the flash point is lowered. A

serious leak in the outer lines may result in a flash of flame, while a small leak in the interior coils is likely to damage the oil being deodorized beyond repair.

Some deodorizers are equipped with a series of cooling coils in the vessel itself. Others are set above a tank (sufficiently large to contain the charge and maintained under high vacuum) in which the cooling coils are installed. Still others are connected to a tubular heat exchanger in which water is the cooling medium. In any event, the finished oil must be cooled to 120–130° F. before it can be exposed to the atmosphere, since rapid oxidation will occur at the temperature of deodorization.

2. Auxiliary Equipment

It is customary to maintain the deodorizers under full vacuum at all times, whether they are in use or not. To hold the vacuum, the low stage of the three-stage ejector is provided with a shut-off valve in the exhaust line. This valve is closed when the deodorizers are down, and the water seal is maintained by the level of water in the three tail pipes in the hot well. Great care must be exercised to prevent any air leaks in the system to avoid the danger of oxidizing the oil, and the deodorizers are carefully tested by observing any increase in pressure during shut-down periods when they are empty.

The blowing steam is superheated to 500–600° F. at a pressure of 10–15 pounds in a superheater which is usually gas- or oil-fired.

Pumps used to empty the deodorizers, or the auxiliary cooling tanks described above, must be capable of pumping out the charge of finished oil against full vacuum.

C. Operation of the Deodorizer

The operation of deodorization is carried out as follows. The deodorizer, under full vacuum, is charged with the stock to be deodorized. The contents are maintained under agitation by cracking steam to the spider, and the temperature is raised to the desired point. This temperature varies considerably, but seldom exceeds 425° F. nor drops below 375° F. Full vacuum will vary from 28.5 to 29.5 inches, depending upon the exhausting system employed. A vacuum of 29 inches or over requires a thermocompressor and a two-stage ejector.

When the deodorization temperature is attained, the blowing steam is turned on. The amount employed will vary inversely with the vacuum. This is obvious, since the higher the latter, the greater will be the expansion of the steam bubbles in rising through the head of oil. Blowing steam consumption is computed in terms of so much steam consumed per pound of deodorized stock over the whole deodorizing period. A maximum of one-half to a minimum of one-tenth has been reported. A fair average

would seem to be about one-quarter pound. Too great a volume of blowing steam will tend to blow over stock into the vapor lines and catchalls, and thus increase the loss. Catchall stock is usually degraded to refinery accumulations, but fat reaching the barometric condenser and hot well is likely to be lost to a considerable degree. The small amount recovered is unsuitable for anything but soapstock or acid oil.

Deodorization is usually complete after 4 to 6 hours of blowing. Little improvement in blandness of the finished stock is noticeable after this lapse of time. Usually winter oil is deodorized for a somewhat shorter period than shortening, since many consumers prefer a definite flavor in this product rather than a completely bland oil. The whole cycle requires 7 to 9 hours, from charging of the deodorizer to pumping out the finished stock.

Cooling water for the barometric condensers often poses a considerable problem to the manufacturer. Spray ponds and cooling towers are frequently used, and the water is continuously recirculated by means of large centrifugal pumps. Both ponds and towers tend to become fouled with fat carried over by the condensed blowing steam, and the water is therefore usually passed through a series of catch basins where as much of the fat as possible is recovered.

During deodorization, especially at a high vacuum, some free fatty acid distills out of the stock, and there is also a tendency toward a further decrease in color. The latter is much more noticeable in the case of compound shortenings and winter oil than with all-hydrogenated shortening. The color drop is probably due to bleaching under heat which is characteristic of cottonseed oil. A winter oil may decrease in color several full Lovibond red units, while an all-hydrogenated product will drop only 0.1–0.2 unit. In the case of winter oil, which is very often sold as a product having a color of 5.0–7.0 red, it is sometimes necessary to add a small portion of very dark refined oil to the deodorizer batch in order to maintain this color in the finished product.

D. Continuous Deodorization

From the foregoing description of the standard batch deodorizer, it is obvious that it is not ideal for the purpose for which it is used. Although the vacuum at the surface of the oil may be 29.5 inches, as the head of oil in the vessel increases the vacuum in the bottom layers may be less than 25 inches. Furthermore, the surface between the steam bubbles and the oil is much smaller at the bottom of the deodorizer than at the top, and unless enough steam is admitted through the spider to keep the contents of the deodorizer violently agitated, removal of odoriferous materials and free fatty acids will require a long time. In any event, the best and most efficient use is not made of either the steam or the vacuum. To overcome

these drawbacks in the batch process of deodorization, the oil being treated should be in thin layers, and, if possible, should move countercurrent to the steam. The bubble tower used for many years in the distillation of petroleum enables these requirements to be met and a continuous deodorizing process [11] has been developed employing a bubble tower instead of a still (see Fig. 187).

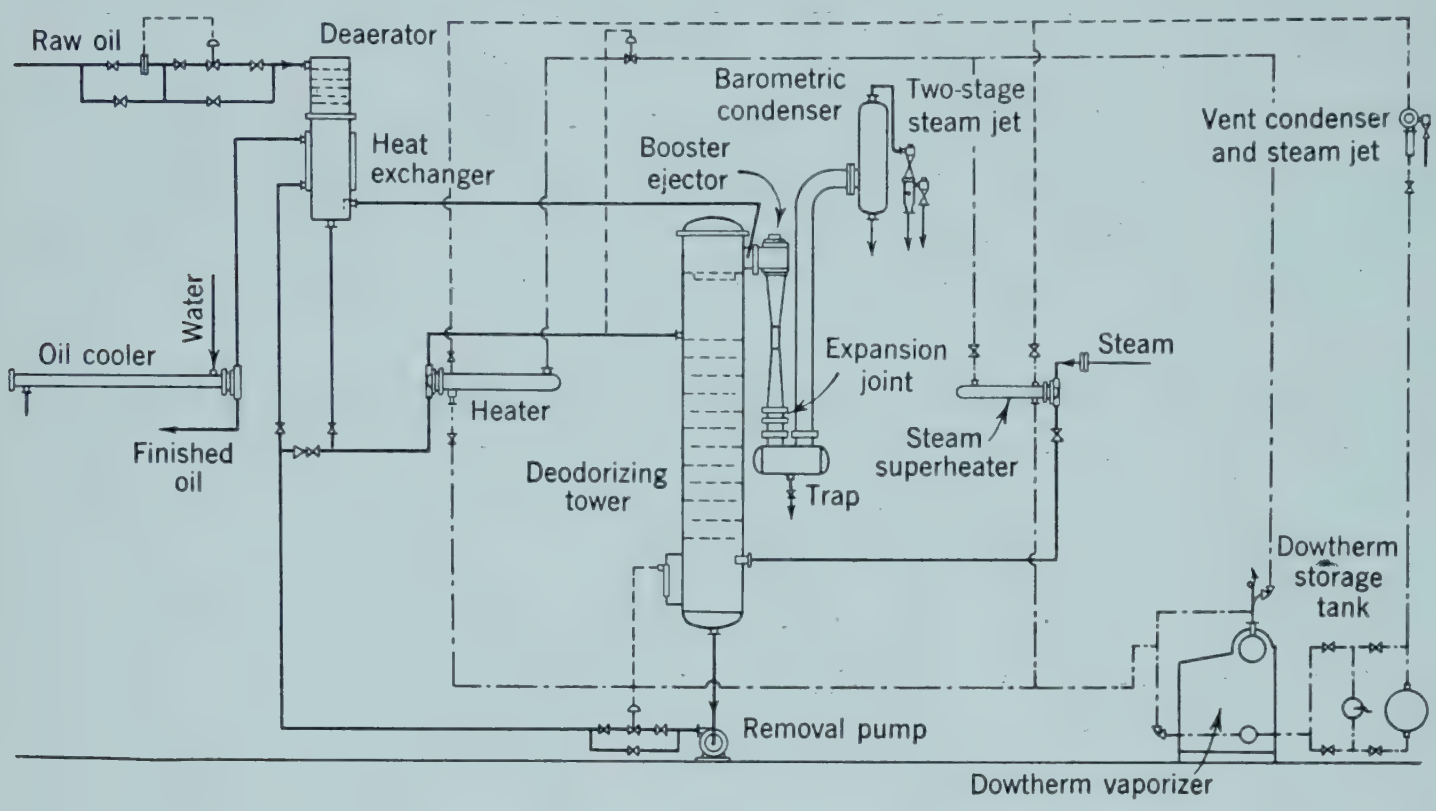


Fig. 187. Flow sheet of continuous deodorization apparatus. (Courtesy *Foster Wheeler Corp.*)

The oil to be deodorized is preheated in a heat exchanger in which a part of the heat is recovered from the finished stock. The exchanger is a vertical tank, the upper part of which is a deaerating chamber. The oil in the exchanger is maintained under full vacuum at all times. The oil passes next to a second heat exchanger—in which the heating medium is Dowtherm vapor—where it is raised to the final temperature. From the second heat exchanger, the hot oil flows to the top tray of a bubble tower, where it meets a rising current of a superheated steam. The oil passes down the tower through a series of bubble trays, in each of which it comes into intimate contact with the blowing steam, which is admitted through a steam ring at the bottom of the tower. The blowing steam is superheated with Dowtherm vapor in a small superheater.

After leaving the last tray, the finished oil collects in the bottom of the tower, where a level of about 18 inches is maintained by means of a float valve. The finished oil is pumped out continuously through the heat exchanger which serves as a preheater for undeodorized oil, and finally through a water cooler in which its temperature is reduced to 140–150° F. It can then be discharged to storage.

[11] E. H. Chapin and D. K. Dean, *Oil & Soap*, **17**, 217–222 (1940).

The deodorizing tower is heavily lagged to minimize heat losses. Its size depends upon the hourly throughput required. The temperature of the oil is 475–485° F. (considerably higher than in the conventional process) and the temperature of the Dowtherm vapor used both for heating the stock and superheating the steam is from 570–580° F. The top of the tower is supplied with a number of baffles to reduce entrainment. A small catch-all or trap is provided from which the steam vapors from the tower pass

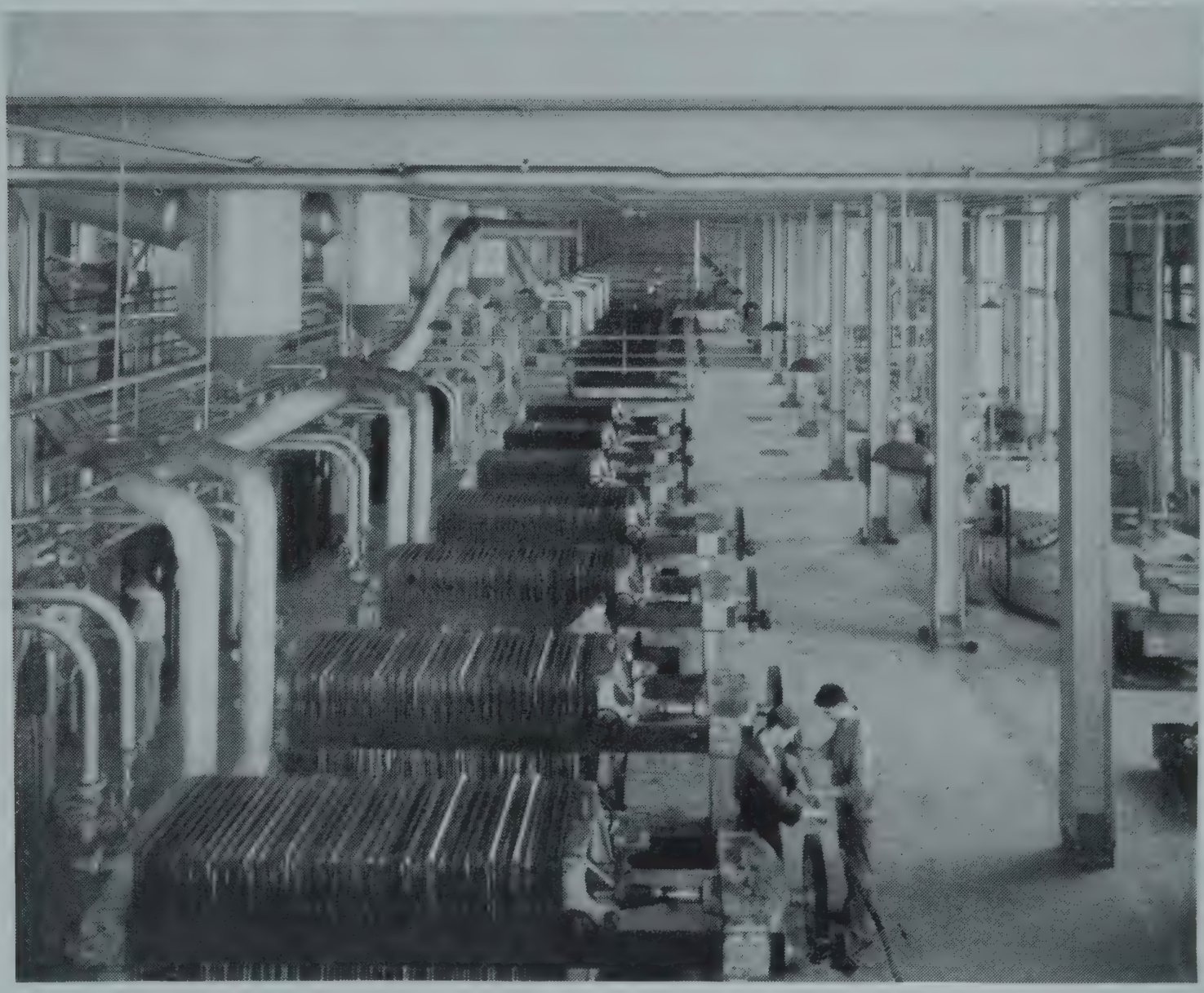


Fig. 188. View of a modern plant for the processing of cottonseed oil, showing deodorizers, converters, bleachers, and batteries of filter presses for earth and catalyst removal and filtration of deodorized oil.

to the barometric condenser, where they are condensed. Practically speaking, deodorization losses are limited to the free fatty acids volatilized from the oil.

The vacuum system consists of a two-stage ejector and a thermocompressor; a vacuum of approximately 28.9 inches is maintained on the Dowtherm preheater for the oil, and 29.75 inches is maintained at the top of the tower. The rise in pressure per bubble tray is approximately 0.06 inch of mercury. Hence, in a tower having ten bubble trays, the vacuum in the last tray would be only 0.60 inch less than at the top. Thus the amount of blowing steam required per pound of stock is much less than in

the regular batch system. Since the vacuum equipment requires 2 pounds of steam for every pound of blowing steam condensed, the economies possible in the continuous deodorizer are obvious. The quality of the shortening or winter oil made in the continuous deodorization process is good. The free fatty acid content is low on account of efficient contact between oil and steam.

A continuous deodorizer, to realize its economies to the full extent, should be operated with the minimum of shut-downs. A unit capable of producing 6,000 pounds per hour of finished stock can be slowed down to about 2,000 pounds per hour without difficulty. This flexibility is very useful in co-ordinating production schedules. Below 2,000 pounds per hour there is a tendency for the stock to go off in quality and darken in color.

When starting up a unit, the time required to bring the whole apparatus to the proper temperature is about 2 hours. It is customary to bring the oil in the preheater-deaerater to a level where the coils are covered and then to circulate the oil through the bubble tower, by-passing the heat exchangers until the deodorization temperature is reached.

Several continuous deodorizers have been installed and are reported to operate satisfactorily.

VI. Finishing Treatment

A. Packaging of Salad Oil

Winter oil, after final filtration immediately subsequent to deodorization, is ready for packing and shipment. It is not customary to store large quantities of deodorized oil in bulk, and common practice is to get the finished oil into packages as soon as possible.

Winter oil is marketed to the retail trade in pint, quart, and gallon containers. During the war, the smaller sizes appeared in glass, although the best and most common containers are sealed cans; 5-gallon cans and 52-gallon (400-pound) drums are also filled for larger consumers, and a considerable portion of the finished winter oil produced is shipped in standard 8,000-gallon tank cars. Standard automatic filling machines are used for packing the smaller containers; the larger sizes are usually placed on platform scales and filled manually.

B. Finishing of Shortenings

Deodorized shortening, despite its increased melting point, is unsuitable for commercial use and must be further processed before it is put into the final package.

1. Solidification of Shortenings

Finished shortening from the deodorizer contains only about 20% of solids at room temperature, hence if it is cooled to 70–80° F., it will form a

mixture of liquid oil and coarse grains of hard fat. Obviously, stock of such characteristics would be unsatisfactory for use either in the kitchen or in the bakery, and it is, therefore, put through a final process known as "finishing." Essentially, finishing is accomplished by rapidly chilling the hardened cottonseed oil to a point below its temperature of solidification and allowing the supercooled liquid to crystallize. Air is usually incorporated in the fat during chilling in order to improve the appearance and plasticity of the finished product.

Two alternative types of apparatus are available for the finishing of shortening; these are open lard rolls and the closed Votator system. The latter has generally displaced the former in more modern plants, but the lard roll is still widely used throughout the industry.

(a) Lard Roll. A lard roll consists of a large, hollow, horizontal, revolving cylinder supported on trunnions and bearings. The roll is cooled by circulating cold brine through the interior or by directly expanding liquid ammonia in the cylinder. At the top of the roll is located a long shallow feed trough through which molten shortening is pumped at a temperature of about 125° F. A thin film of the liquid fat is picked up by the roll from the feed trough, and as the revolution of the roll continues, the fat is partially solidified. Just below the feed trough, the semisolid shortening is cleanly scraped from the roll by means of a long knife blade. Shortening is in contact with the cooled surface of the roll for approximately 7 to 8 seconds. The thin layer of partially solidified fat scraped from the roll is about $\frac{1}{32}$ inch in thickness and its temperature is 40–60° F. A standard lard roll is approximately 9 feet long and 4 feet in diameter and has cooling surface for shortening of 108 square feet. Under conditions of normal operation, the shortening is cooled at a rate of about 0.115 pound per square foot of cooling surface per minute.

During the chilling, a portion of the shortening is supercooled sufficiently to cause very rapid crystallization. The latent heat released by this partial crystallization is absorbed by the cooling medium in the roll, which is one of its most important functions.

The chilled fat drops from the knife blade into a "picker box." The picker box consists of a long horizontal U-shaped trough through which passes, lengthwise, a revolving shaft. Flat blades are set in the shaft at such an angle that the shortening will be propelled toward the outlet of the trough. The level of stock in the picker box is maintained at a point which allows a substantial portion of the blades to be exposed. Thus, through the revolution of the blades, air is continuously whipped into the shortening. The amount of air incorporated is controlled by the speed of the shaft, the distance which the blades extend above the surface of the fat, and the pitch of the blades.

Since crystallization of the shortening on the roll is incomplete, as

crystallization continues during its passage through the picker box additional heat is released. The temperature of the fat, which is 40–60° F. on leaving the roll, will have risen to 70–80° F. at the outlet of the picker box.

A steam pump is usually employed to remove the shortening continuously from the first picker box and deliver it to a second, and at the same time to build up pressure on the shortening to 150–400 pounds gage. The stock is released into the second picker box through a valve of the homogenizing type. The operation of building up the pressure on the shortening and then releasing it to atmospheric pressure is what is meant by the term "texturization," because the operation is conducted for the purpose of obtaining a smooth and uniform texture.

The second picker box is much like the first, but the level of the fat is controlled to keep the revolving blades covered at all times. The purpose of this second trough is to allow the fat additional time to complete its crystallization, with release of the balance of its latent heat, and to break up any lumps which may be present. The shortening is removed from the second picker box by another steam pump, the pressure being again built up and again expanded to atmospheric pressure through a second valve.

Were the shortening merely chilled rapidly without the inclusion of air, it would set up to a translucent mass of unattractive appearance. The incorporation of air, however, causes the shortening to be white and opaque, as it appears in the finished package, and also renders it more plastic.

During the texturating step, the air whipped into the shortening in the first picker box is dissolved to some extent in the fat at the high pressures employed. Sudden release from this high pressure to atmospheric pressure results in a very fine and thorough dispersion of tiny air bubbles throughout the shortening.

Shortening can be packed directly from the first picker box, but the texture obtained through such a single treatment is not so smooth and uniform as when it is texturated twice. Since crystallization of the shortening is largely completed when it passes to the second picker box, there is little subsequent rise in temperature of the fat beyond this point in the process. In order to improve the texture and packing properties, it is a practice in some plants to raise the final temperature of the shortening by applying heat to the fat in the first picker box pump. Some of the solidified shortening is melted, and as a result, the feed to the second picker box will contain free oil. However, due to the continued agitation, the discharge from the second picker box will be a homogeneous product.

(b) The Votator. Votators are supplanting lard rolls for the finishing of shortening in the more modern plants. The Votator machine was originally developed for use in the manufacture of ice cream, and while the general object of rapid cooling of the shortening is the same as with

the lard roll, the details by which this result is effected are radically different (see Fig. 189).

Melted shortening is pumped into a feed tank at a temperature of 125–140° F. From the feed tank it is picked up by a rotary positive displacement pump which conveys it to the chilling equipment. Air is

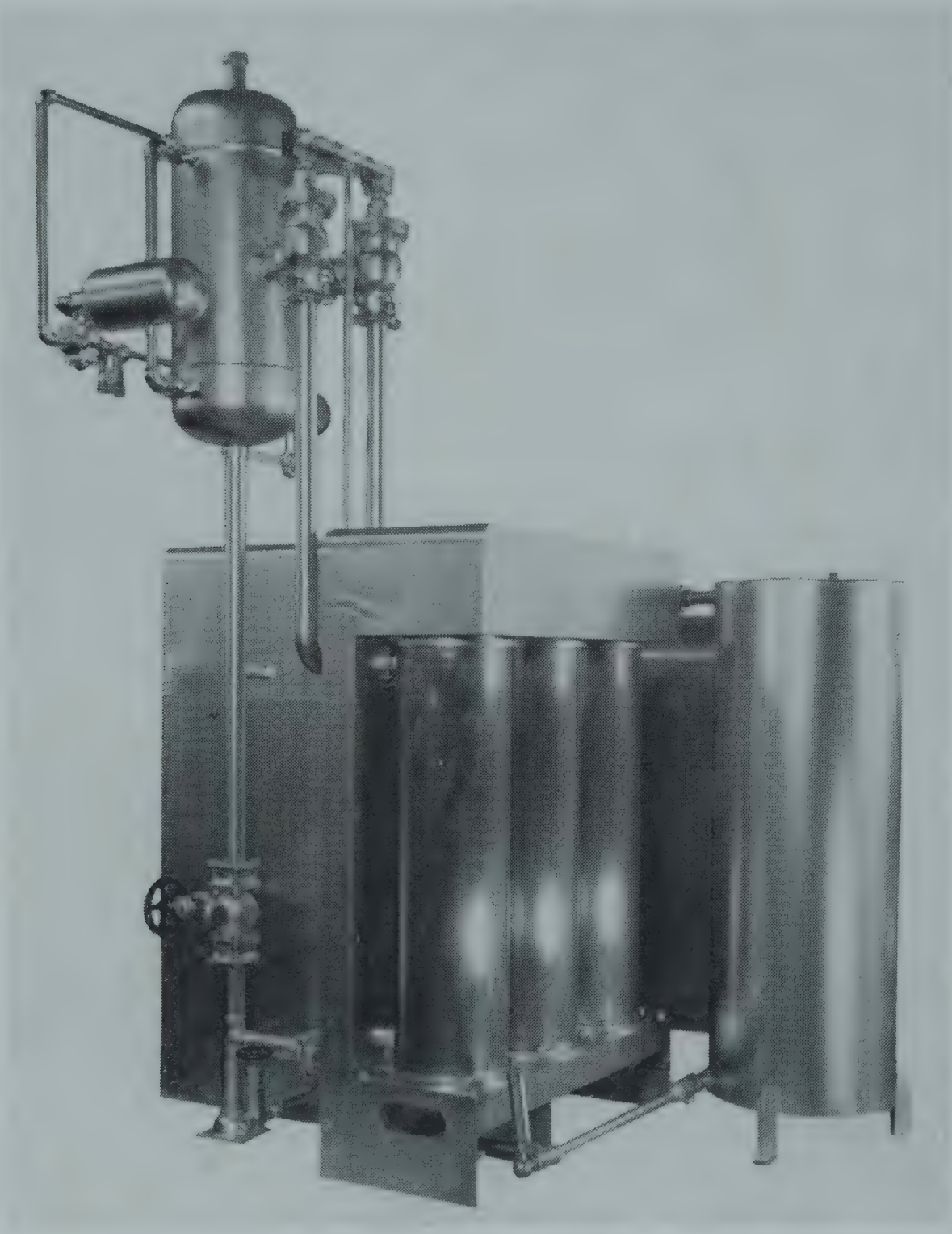


Fig. 189. Votator for shortening solidification.
(Courtesy *The Girdler Corp.*)

drawn into the liquid fat on the suction side of the pump—the amount being controlled by a needle valve in the line.

The chilling element, known as the "A" unit, consists of one or more relatively small tubes, each of which is supplied with an agitator, the latter almost filling the tubes and leaving a very small annular space for the passage of the fat. A refrigerant (liquid ammonia) circulates about the outside of the tube. As the aerated shortening under a pressure of

300 to 400 pounds per square inch passes through the tubes, the film of fat constantly formed on the surface is removed by small blades on the agitator shaft and thus new material is continually exposed to the cooling surfaces. The total cooling surface of the usual commercial Votator is less than one-tenth that of a standard lard roll, but the cooling ratio, expressed in pounds of stock per minute per square foot of cooling surface, is much greater. This difference in cooling surface and ratio is largely overcome by the use of agitation under pressure in the Votator. Despite the difference in cooling surface ratio, the amount of supercooling in the Votator is approximately equal to that in the lard roll.

However, because of the short time the shortening remains in the tubes, considerably less latent heat is removed in the Votator than in the lard roll. This is shown by the fact that the temperature of stock leaving the Votator is considerably higher than that leaving the surface of a lard roll.

The Votator also has an enclosed picker box which is called the "B" unit. Its purpose is to allow further time for crystallization of the shortening with consequent dissipation of the latent heat of crystallization. The "B" unit is under the same pressure as the "A" unit, and the stock on leaving the former is expanded to atmospheric pressure through an extrusion valve. The "A" unit may be likened to the lard roll and the "B" unit to the first picker box. The stock may be packed directly from the "B" unit, but in many installations a second "B" unit is provided in order to allow a longer time for crystallization before passing the shortening into the package. The temperature at which Votator-processed stock is delivered to the package is approximately 75–90° F. This is about equal to the temperature of roll chilled shortening that has been heated in the first picker box pump. The higher temperatures resulting from the Votator are due to the fact that the cooling medium absorbs less of the heat of crystallization than is absorbed by the refrigerant in the lard roll, because of the shorter time interval involved.

2. Packaging of Shortenings

Finished texturated shortening for commercial use is usually packed in 50- or 100-pound tins or in 400-pound removable-head steel drums. For home consumption, the shortening is packed in 1- and 3-pound cans, in 1-pound cartons or prints, similar to the familiar butter package, or occasionally in larger cartons.

Shortening packed in the larger containers (50 pounds and larger) is generally passed directly from the texturating valve of the roll or Votator to the tared drums or tins which are set on platform scales and are filled to the desired weight.

(a) Filling Machines. Household shortenings are usually packed in

the smaller cans by a packing machine of the volumetric type. Machine of two types are in general use. In the first machine, the shortening expanded directly through the texturating valve of the second picker bo following the lard roll, or the "B" unit of the Votator, into a hoppe A revolving plate forces the texturated shortening from the hopper int cylinders, whence it is in turn passed into the cans. The filler is so con structed that differences in the air content of the shortening can b compensated for, by changes in the length of the filling cylinder.

The second filler operates upon a somewhat different principle whic may be described as follows. A horizontal filling cylinder is charged wit stock directly from the pump at the second picker box after the roll, o from the "B" unit of the Votator, under pressure. The cylinder has a inlet and an outlet at either end, and is traversed by a piston, the length of whose stroke is adjustable. The neutral position of the piston is in th center of the cylinder, thus in effect dividing it into two. Shortening enter the left-hand inlet under pressure from the pump, the left-hand outle being closed. At the same time, the right-hand inlet is closed and th right-hand outlet is open. The entering stock moves the piston to the right and shortening is discharged from the right-hand outlet into the can through a special slot-valve with which the machine is fitted. This valve serves to texturate the shortening in a manner similar to the valves pre viously mentioned. When the piston has reached the end of its travel, the right-hand outlet automatically closes and the right-hand inlet opens. Simultaneously, the left-hand inlet is closed and the left-hand outlet opens. The piston moves to the left under pressure of feed stock entering through the right-hand inlet, and shortening is forced from the left-hand outlet through another slot valve into a second can, and so on. The distance which the piston is set to move is, of course, dependent upon the size of the container being filled.

During World War II, it was necessary to pack a considerable amount of shortening in glass, but the above-mentioned filling machines proved adequate to cope with this material. After they are filled, the containers pass through a sealing machine in the case of tin cans, or a capping machine when glass jars are used. Fillers of the second type are commonly employed for the packing of shortening sold in prints.

After the containers have been filled and sealed, they are stored in a warehouse so that the contents will be completely set before shipping the shortening.

(b) Stability in the Package. Prior to the development of modern methods of processing and packaging, a great deal of difficulty was experienced because of the deterioration of the shortening in the field before reaching the consumer. The shortening was unstable with respect to the development of rancidity and off odors and flavors. The appearance

deteriorated after a short time in storage, because of the loss of dispersed air. Improved methods of processing, particularly hydrogenation and deodorizing, have greatly extended the stability of the shortening against rancidity. A notable improvement has also been made in packaging through the use of hermetically sealed cans which protect the product from atmospheric conditions. As a result of these advancements, a properly processed shortening packed in sealed cans will readily keep a long time under conditions usually encountered in distribution channels, so that the consumer is now assured of receiving the product in practically as good a condition as when manufactured.

CHAPTER XVIII

EDIBLE COTTONSEED OIL PRODUCTS

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I. Introduction

Most of the cottonseed oil produced in the United States has always found its way into edible products. The purpose of the present discussion is to treat the edible products derived from cottonseed oil in some detail, with the history and statistics of the edible industry being considered only where this is necessary for continuity and completeness in the discussion. The latter subjects are covered in detail in earlier chapters of this book.

A. History and Effect of Processing Improvements

Until 1870, cottonseed oil of edible quality was produced only experimentally.[1] However, in the following two decades, production increased rapidly. Large quantities were used in soap, and some found its way into cooking and salad oils. However, the refining techniques of that time were unsatisfactory and incapable of producing edible oil of entirely acceptable quality. Crude cottonseed oil is unsuitable for use in food because of its dark color, high free fatty acid content, and objectionable odor and flavor. It was necessary to develop methods of improving it with respect to these properties before any large quantity could be utilized edibly.

Acid refining techniques were introduced at the last of the eighteenth century but never assumed importance. During the 1840's, alkali refining procedures using calcium and potassium hydroxides were developed in Europe. Alkalies were not employed in this country until the 1880's, when the use of caustic soda was introduced in refining. The action of caustic alkali is to remove the free fatty acids and a large proportion of the pigments. It was found that such refined oil could be used for packing sardines and for mixing with lard, the original shortening agent. The

[1] The reader is referred to G. M. Weber and C. L. Alsberg, *The American Vegetable Shortening Industry*, Stanford Univ. Press, Stanford Univ., Calif., 1934, for a complete history of the economic, technological, and regulatory factors affecting the growth of the industry.

latter practice was carried on particularly when lard was scarce and expensive.

Further removal of color from cottonseed oil was necessary to make the oil altogether acceptable for edible purposes. The first bleaching of cottonseed oil intended for edible uses was accomplished by exposing the oil to sunlight in tanks on factory roofs. The method was costly and unsatisfactory, particularly because the oil deteriorated in keeping quality. Carbon in various forms was the first adsorbent bleaching agent used but it was replaced during the latter quarter of the nineteenth century by various clays or bleaching earths first imported from Europe. Later, deposits of bleaching earth were discovered in Florida, Georgia, Mississippi, Arkansas, Texas and California. The lighter colored oils produced by the use of these earths could be used to a larger extent in blended shortenings without adversely affecting the color.

To counteract the softening effect of cottonseed oil on lard, tallow or oleostearin was added; thus, in reality, the first blended shortenings were introduced. By the middle of the 1880's, the so-called "compound lard" or "compound" appeared on the market. Later, shortenings were prepared from oleostearine and cottonseed oil. Also, some cottonseed oil was used in margarine.

By 1890, the blended shortening industry was well established. Even though alkali refining and bleaching removed some of the odors of cottonseed oil, the oil still retained an odor and flavor which detracted from its utility in shortening and margarine. The latter products were characterized by the flavor of the meat food fats chiefly used in their formulation. The first deodorization was carried out in the 1890's by blowing steam through the oil heated to 340–350° F. The volatile odors and flavors were thus removed to a certain extent, but it remained for the vacuum deodorization process of David Wesson to yield an entirely bland oil, which was also markedly improved in keeping quality. This resulted in the production of shortenings and cooking and salad oils of greatly improved quality, for which the demand increased. However, shortening manufacturers were forced to rely on the harder meat food fats—edible tallow and oleostearine—as stiffening agents. As a result, the greater proportion of the blended shortenings was manufactured by the larger meat packers. The meat food fats were the only source of the hard saturated glycerides which were necessary to impart the required firmness and consistency and cause the shortening to remain solid at ordinary temperatures. It remained for the development of the hydrogenation process in the first decade of the twentieth century to provide hard glycerides from liquid cottonseed oil. In this process, hydrogen under the influence of a nickel catalyst adds to the double bonds of the liquid unsaturated fatty acids of cottonseed oil (oleic and linoleic), converting these acids to solid stearic acid. The

net result is a solid fat. When it is blended with unhydrogenated oil in the required proportions, a plastic shortening, solid at room temperature, is produced.

In addition to increasing the melting point of the oil, hydrogenation increases its stability or resistance to oxidation. A considerable increase in stability occurs before saturation is reached. This circumstance led to the development of the so-called all-hydrogenated shortenings, in which liquid oil is hydrogenated until a large proportion of the linoleic acid is converted to oleic acid and the melting point is increased to between 90° and 100° F. To this partially hydrogenated mass is then generally added a small amount of substantially completely hydrogenated oil to further raise the melting point and impart plasticity. Such products have many desirable properties in addition to high stability, which make them acceptable for general shortening and frying purposes.

Thus, with the advent of hydrogenation, the all-vegetable shortening industry was born. The meat packers continued to use meat fats and hardened oil, while the other manufacturers employed only the hardened oil. The latter developed products which were marketed in direct competition to lard and blended shortenings.

The production of smooth, plastic compounds containing beef fat and lard or hydrogenated cottonseed oil posed some problems. Agitating the mixtures in chilled tanks, the method that had been used for lard, resulted in grainy products, because the stearin separated first in large crystals. This was overcome by chilling the mixtures rapidly on refrigerated rolls and then pumping the chilled fat through orifices into packages.

B. Properties of Cottonseed Oil

Although the properties of cottonseed oil are discussed in detail in an earlier chapter (Chapter VII), some of the characteristics which make it highly acceptable as an edible oil deserve elaboration here.

1. Miscellaneous Properties

Even though cottonseed oil is darker in color than soybean, peanut, and corn oils—its principal domestically produced competitors—the pigments of the oil are readily removed by modern refining and bleaching techniques, so that edible products produced therefrom possess the lightness of color demanded by present-day consumers.

Cottonseed oil also possesses properties which make it satisfactory for processing into salad oil. The proportion of highly saturated glycerides is such that when the oil is slowly chilled the higher melting glycerides separate and can be readily removed by filtration, leaving an oil which will not crystallize when held at temperatures of 40° to 45° F. Such oils find great utility as salad oils used for the manufacture of salad dressings,

mayonnaise, French dressing, etc. The stearin or higher melting portion is generally utilized in blended shortenings or in hydrogenated products.

Cottonseed oil is readily hydrogenated. After it is properly refined and bleached, hydrogen adds to the double bonds with great facility, if no materials are present normally which poison the catalyst or adversely affect the course of the reaction. Any desired amount of hydrogen up to that representing complete saturation may be added, to produce a melting point of any degree desired from that of the liquid oil up to 140° or 150° F.

2. Stability

Probably the most important of the outstanding characteristics of cottonseed oil is its stability. It contains only traces of fatty acids with unsaturation greater than that of linoleic acid. The highly unsaturated acids are more susceptible to attack by oxygen, while oleic and linoleic, which make up the unsaturated acids of cottonseed oil, are less readily oxidized. Refined and bleached cottonseed oil may be thoroughly deodorized and will resist rancidity, if carefully packaged, for periods in excess of the time normally required for movement through commercial channels. During hydrogenation, a large part of the linoleic acid is converted to oleic or stearic acid and the stability is further increased. Hydrogenated cottonseed oils with a melting point of 100° F. or higher show extremely good keeping qualities, as measured by accelerated oxidation tests, and actually hold up for many months without the development of any perceptible rancidity.

In addition to the resistance of cottonseed oil—particularly after hydrogenation—to the development of rancidity, this oil has markedly less tendency than certain of its competitors to undergo another type of deterioration, commonly referred to as flavor reversion. This is the development, after complete deodorization, of an undesirable odor and flavor different from that caused by rancidity. The term is actually a misnomer, since the flavor and odor that develop are usually different from the original odor and flavor. Comparatively little is known of the chemistry of this type of deterioration, but oil chemists and technologists generally agree that it is a result of oxidation or is at least associated with this phenomenon.

The stability of cottonseed oil, as well as that of the other vegetable oils, is due to the small amounts of substances it contains that are capable of inhibiting oxidation markedly. The vegetable oils are in general much richer in their content of these materials than are the animal fats. Mattill [2] has pointed out that nearly all materials that have antioxidant properties are ortho- or para-, di- and polyphenolic compounds. Also, some compounds whose molecules have an electronic configuration similar to these

[2] H. A. Mattill, *Oil & Soap,* **22,** 1–3 (1945).

phenols are antioxidants.[2] It is known that certain types of phenolic compounds occur in cottonseed oil in small quantities. The most abundant of these seem to be tocopherols, which are the compounds having vitamin E activity. Olcott and Emerson [3] showed them to be effective antioxidants. Three of these compounds exist in nature. Olcott and Emerson have shown the gamma form to be the most powerful antioxidant of the three, with the beta and alpha forms less effective, in that order.

Gossypol, a highly complex chemical compound occurring in crude cottonseed oil, has been shown by Royce [4] to have strong antioxidant properties. However, this compound is completely removed by alkali refining and is not carried into the edible products. Also occurring in crude cottonseed oil are phosphatides, but these alone exert no antioxidant effect in vegetable oils.

The resistance to oxidation of cottonseed oil and cottonseed oil shortenings can be increased by the use of the acidic type of antioxidants, which act synergistically with the phenolic substances in the oil.

C. Utilization of Cottonseed Oil

In 1944, less than 0.1% of the cottonseed oil consumed was used in the crude form; all of the remainder was refined, and only about 0.5% of the refined oil was used for other than edible products. Refined cottonseed oil is used in shortening, cooking and salad oils, margarine, and other products, such as coating and filler fats, and shortening extenders. Table 180, compiled from data published by the United States Bureau of the Census, shows the amounts of cottonseed oil used in these various products in 1944.

TABLE 180

Cottonseed Oil Used in Various Edible Products in 1944[a]

Product	Production, 1000 pounds
Shortening	489,880
Cooking and salad oils	327,987
Margarine	215,007
Other products	34,343
Total	1,067,213

[a] From *Animal and Vegetable Fats and Oils*, U.S. Bureau of the Census, 1945.

The amount of cottonseed oil used in shortening and margarine in 1944 in relation to the total utilization of oils and fats is indicated in Table 181.

[3] H. S. Olcott and O. H. Emerson, *J. Am. Chem. Soc.*, **59**, 1008–1009 (1937).
[4] H. D. Royce, *Oil & Soap*, **10**, 123–125 (1933).

Table 182 shows the percentages of the various oils and fats used in hortening in the years 1940–1944.

TABLE 181

Amount of Cottonseed Oil and Other Oils and Fats Used in Shortening and Margarine in 1944[a]

Oil used	In shortening, pounds	In margarine, pounds
Total oils	1,309,039,000	475,076,000
Cottonseed	489,880,000	215,007,000

[a] From *Animal and Vegetable Fats and Oils*, U.S. Bureau of the Census, 1945.

TABLE 182

Percentages of the Individual Fats and Oils Used in Shortening[a]

Fat or oil	Use, %				
	1940	1941	1942	1943	1644
Cottonseed	68.8	62.7	54.0	41.7	37.4
Soybean	17.7	15.5	26.1	41.5	47.4
Peanut	1.9	5.8	2.9	3.7	4.7
Other domestic oils	0.1	—	0.3	1.0	0.4
Other foreign vegetable oils	4.4	7.7	4.7	0.4	0.4
Edible tallow	3.3	2.9	4.3	5.7	4.6
Oleostearin	1.4	1.6	2.4	2.2	1.7
Lard	1.4	3.6	4.8	2.7	2.9
Fish oils	0.9	0.4	0.4	0.9	0.2
Other animal and marine oils	0.1	0.1	0.1	0.2	0.2
Total	100.0	100.0	100.0	100.0	100.0

[a] From *The Fats and Oils Situation*, Bureau of Agricultural Economics, July, 1945.

II. Shortenings

Shortenings are generally defined as semisolid plastic materials made wholly from fats and oils. They are used in cooking, baking, and frying.

The data in Table 180 indicate that nearly half of all the cottonseed oil is used in the manufacture of shortening. The people of the United States, being mostly of northern European extraction, have been accustomed to solid fats of animal origin, and consequently prefer solid shortening materials in contrast to the liquid oils used predominantly by peoples of southern European or Asiatic origin. In 1944, of the per capita civilian consumption in the United States of edible fats and oils amounting to 42.3 pounds, shortening constituted 9.2 pounds and lard 13.9 pounds.

The average consumption of butter fat was 9.5 pounds and, of fat in the form of margarine, 3.1 pounds, leaving 6.6 pounds as the consumption of other forms of fat, such as salad and cooking oils.[5]

It has been mentioned previously that shortenings were originally developed in America as a direct result of the growth of the cottonseed industry. The large amount of cottonseed oil which became available during the latter decades of the nineteenth century as a by-product of cotton provided the essential raw material.

A. Classification of Shortenings

There are two general classes of shortenings. The first is the blended type, which may be subdivided into: (*a*) all-meat fat shortenings; (*b*) all-vegetable shortenings; and (*c*) blends of meat fat and vegetable oils. This classification is based on the raw materials used. Government regulations require that, if more than 50% meat fat is used, the label must read "Made from animal and vegetable fats." On the other hand, if the formula contains over 50% vegetable oil, the label must read "Made from vegetable and animal fats." The second class of shortenings is the all-hydrogenated. These may be divided on the basis of their intended use as: (*a*) all-purpose shortenings, (*b*) biscuit and cracker-type shortenings, (*c*) emulsifying-type shortenings, and (*d*) frying fats, etc.

The blended-type shortenings were the first to be manufactured. In these, the oils and fats are usually refined and bleached separately and then blended into the mixture in the proper proportions. The mixture is deodorized, chilled, and packaged. This type of shortening finds its way largely into household use, particularly in the southern United States, but it is also widely used in commercial establishments.

There are some important differences between the blended and the all-hydrogenated shortenings. One of these is a marked difference in stability. Since hydrogenation reduces to a large extent the content of highly unsaturated acids, the all-hydrogenated product is considerably more resistant to oxidation. Without the use of antioxidants, about 40 hours in the Swift test is the maximum stability to be expected from blended shortening. On the other hand, hydrogenated shortenings with stabilities up to about 200 hours are quite easily produced.

Another point of difference is the greater plasticity of the blended shortenings. The matter of plasticity and consistency will be dealt with later, but it suffices to say here that the greater the difference in melting point between the components of a shortening, the greater will be its plasticity. Therefore, when hydrogenation is carried to the point of a considerable reduction in unsaturated fatty acids, with consequent increase in the melting point, the difference in the melting point between the main

[5] *The Fats and Oils Situation*, Bureau of Agricultural Economics, July, 1945.

portion of the product and the hard fat which is added is decreased and less plasticity or a shorter plastic range results. However, by careful control of the hydrogenation conditions, it is possible to carry hydrogenation to the point where both excellent stability and plasticity are obtained.

The all-hydrogenated shortenings also have somewhat better creaming quality than do the blended shortenings.

B. Properties of Shortenings

1. Physical Properties

(a) Microscopic Structure. To ordinary visual observation a shortening appears to be a homogeneous solid. However, microscopic examination reveals it to be a mixture of liquid oil and small, separate, discrete crystals. The accompanying photomicrograph (Fig. 190) reveals the

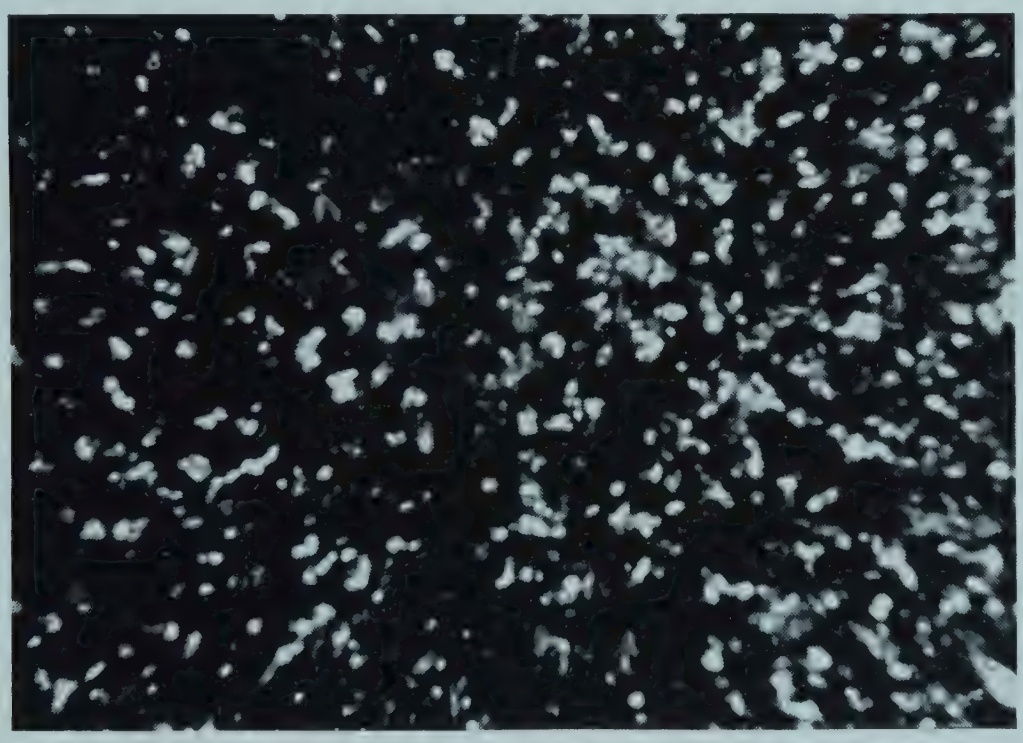


Fig. 190. Photomicrograph (×1,350) of hydrogenated vegetable oil shortening.

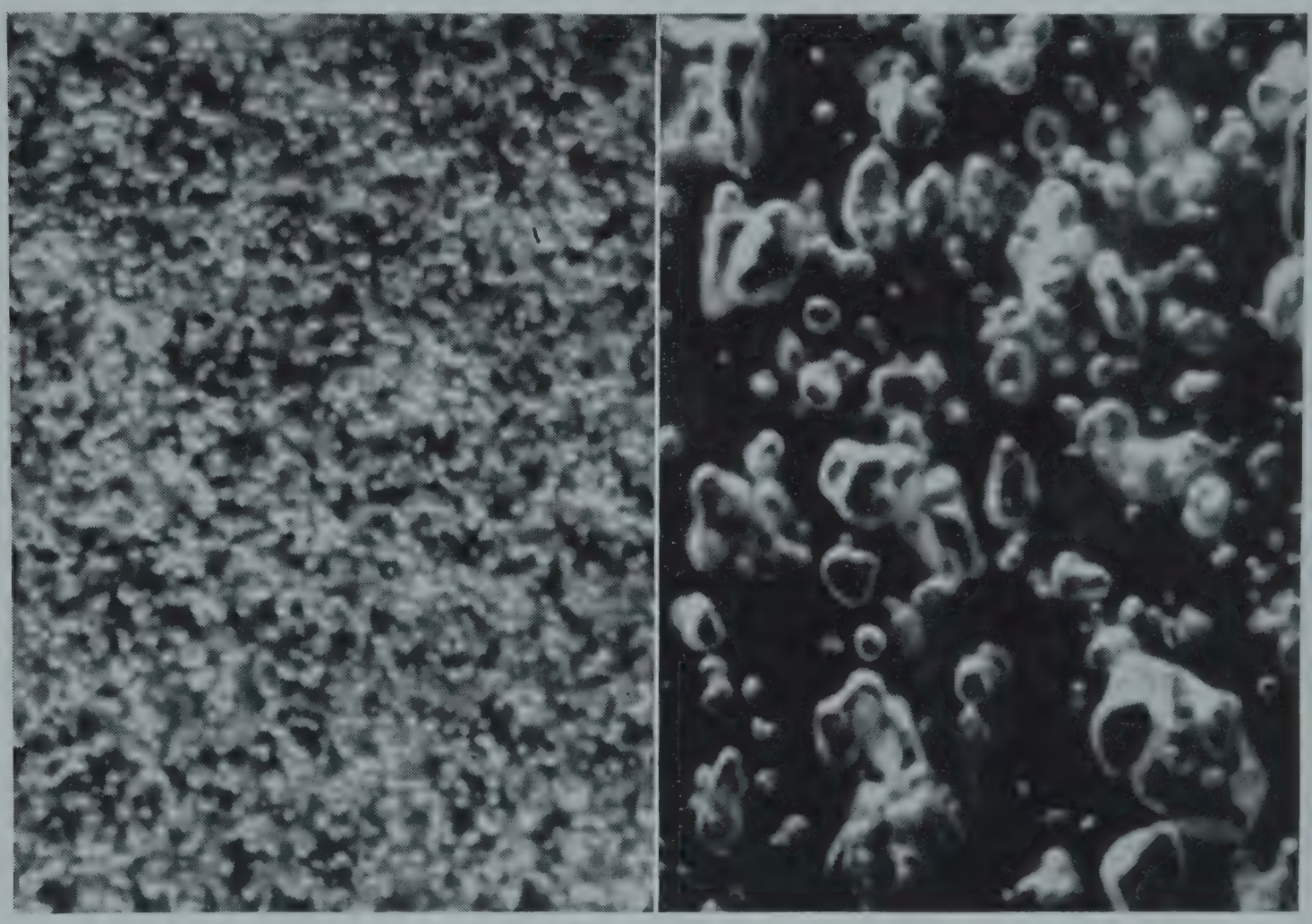
crystalline nature of portions of a hydrogenated vegetable oil shortening. Liquid oil fills the spaces between the crystals. Shortenings are plastic solids, *i.e.*, they behave as solids and retain their shape when subjected to small stresses, but flow when subjected to larger stresses. Bingham [6] has pointed out that the distinctive properties of plastic solids are due to the tendency of the solid particles to form matrixes which support it against stresses. When sufficient force is applied, the matrix breaks and the material flows. The greater the proportion of solids to liquid, the more opportunity there is for the solids to interlock and the firmer is the material. Also, the finer the solid particles, the more opportunity there

[6] E. C. Bingham, *Fluidity and Plasticity,* McGraw-Hill, New York, 1922.

will be for them to touch, resulting in increased friction—and more force will be required to cause flow.

(b) Consistency. The consistency of fats is measured empirically and the results are expressed in arbitrary units. Penetration methods are commonly used, but nearly every shortening manufacturer uses a different instrument and scale.[7]

The consistency of fat varies greatly with temperature, the fat becoming softer as the temperature increases, and firmer as it decreases. This is



(a) (b)

Fig. 191. Photomicrographs (×90) of vegetable oil shortenings showing (a) good distribution of air and (b) poor distribution of air.

due to the fact that fats contain a large number of different glycerides, each of which has a distinct, and in most cases a different, melting point. As a result, there is a definite temperature below which each glyceride tends to be solid and above which it tends to be liquid. Above their melting points, the glycerides are mutually soluble. Even below their melting points, they are partially soluble one in the other. This results in a gradual transition from liquid to solid and *vice versa,* as the temperature is varied, instead of the sharp melting characteristic of pure compounds. At the lower temperatures, a larger proportion of the glycerides is solid and the fat is firmer. At the higher temperatures, a larger proportion is liquid and the fat is softer. Also, the greater the differences in the melting

[7] A. D. Rich, *Oil & Soap,* **19,** 54–57 (1942).

point of the glycerides making up the fat, the greater will be the range of temperature over which the product does not become too firm or too soft.

If liquid fats are cooled rapidly, supercooling takes place and the fats will be softer than if equilibrium exists. As the temperature of the supercooled fat is raised, the glycerides pass through various unstable polymorphic forms, sometimes passing through liquid phases between the various crystalline forms.[8] When the temperature has been raised above the melting point of the unstable forms, the glycerides change into their highest melting stable form. Subsequent cooling of this form does not alter the melting point. However, if a fat is melted and cooled slowly, larger crystals will form and the product will be softer than when it is when chilled rapidly (with the formation of small crystals). "Plastic range" is a term commonly used to designate the temperature range within which a shortening is workable.

Manufacturers take advantage of these peculiarities in the physical properties of fats in their processing operations. Shortenings are supercooled when chilled on chill rolls or in the more modern internal chilling machines. The sensible heat and some of the latent heat of crystallization are removed. However, enough of the latter is allowed to remain to produce a temperature rise. The temperature is allowed to rise until most of the solid glycerides are converted to a higher melting, although not necessarily, most stable form. To insure the proper amount of conversion to the higher melting form, shortenings are generally tempered, *i.e.*, held at a temperature above which the transition to the higher melting forms takes place. This handling results in a product with fine crystals that will withstand cooling to low temperatures without appreciable change in crystalline form, and which will retain its plasticity.

(c) Incorporated Air. Nearly all shortenings on the market contain 10 to 20% by volume of air or other gas. The air is finely dispersed and appears as small bubbles, easily discernible under the low-power microscope, as indicated in the photomicrographs of Figure 191. These air bubbles are claimed by some manufacturers to enhance the creaming qualities of the fat. It is the goal of shortening manufacturers to obtain fine dispersion of the air. This improves the appearance of the shortening, making it creamy white in contrast to a yellowish cast characteristic of Vaseline when no air is present. Even distribution of the air in small bubbles greatly improves the whiteness and appearance of the shortening.

2. Chemical Properties

There are several chemical properties of shortening which are important factors in their utilization and which deserve consideration here.

(a) Free Fatty Acid Content. The content of free fatty acids has always been an important index of the quality of a fat. In a shortening,

[8] R. H. Ferguson and E. S. Lutton, *Chem. Revs.*, **29,** 355–384 (1941).

it is an indication of the efficiency of the refining and deodorization processes. Generally speaking, the lower the free fatty acid content, the better is the deodorization, consequently, the better are the odor and flavor. Free fatty acids are determined by direct titration of the fat with alkali.

(b) Smoke Point. The smoke point is dependent on the free fatty acid content and varies inversely with it. A smoke point above 400°F. is generally considered satisfactory. The smoke point is determined by heating a given quantity of the fat under definite conditions and observing the temperature at which the first wisp of smoke is visible under certain conditions of lighting.

(c) Iodine Number. The iodine number is a measure of the unsaturation of a fat or shortening. The higher the iodine number, the greater is the content of unsaturated fatty acids. It is determined by measuring the amount of iodine or other halogen absorbed by a given quantity of the fat in a definite length of time.

(d) Color. Properly speaking, color is a physical, rather than a chemical, property. However, it is commonly included among the properties regularly determined in chemical laboratories. The color of a shortening product is considered an index of quality. Generally, the lighter the color reading, the whiter will be the appearance of the plastic shortening and margarine. Present standards in the industry call for colors not darker than 2.5 red as measured on the Lovibond scale.

(e) Flavor. The flavor depends on the type of raw materials used in a fat product and on the efficiency of the deodorization process. In deodorized products, complete blandness or absence of flavor and odor is the only acceptable standard. It is evaluated only by tasting, and the ability to judge samples accurately by taste is acquired only after considerable experience.

(f) Stability or Keeping Quality. This factor is a measure of the resistance of the fat to the development of rancidity. It is measured by several accelerated methods. One of the most common is the Swift stability method, which consists of passing air through the fat as it is held at a standard temperature and measuring the time until rancidity, as measured by increase in peroxides, develops. This time is expressed in hours A.O.M. (active oxygen method). Generally, the higher the A.O.M., the longer a fat will keep before rancidity develops. However, the ratio of A.O.M. to actual shelf life varies somewhat from product to product.

(g) Initial Peroxide Value. This property is a measure of the incipient oxidation which results in rancidity. When oxygen attacks fats, peroxides are formed and gradually build up until the fat breaks down at the oxidized linkages, with the formation of rancid-smelling materials. The lower the initial peroxide value, the less oxidation has taken place.

It is determined by titrating the iodine liberated from potassium iodide by a given quantity of the oxidized fat.

C. Composition and Characteristics of Shortenings

1. Blended Shortenings

(a) Blended Shortenings from Meat Fats and Vegetable Oils. Since this type of shortening is made under the inspection of the U.S. Department of Agriculture, it is practically all produced by meat packing companies. The original product varied in composition, but one of the standard formulas used for many years consisted of about 80% refined and bleached cottonseed oil and about 20% of oleostearine. Later, other vegetable oils and meat food fats, such as tallow and lard, were incorporated. Today, with the aid of modern control techniques and processing methods, the formulation may be varied over wide ranges, and shortening of uniformly high quality produced. The only fundamental requirement is to provide the proper ratio of saturated to unsaturated glycerides, which is necessary to obtain the desired consistency and plasticity. The saturated glycerides may be obtained from oleostearin, hydrogenated tallow or lard, or hydrogenated vegetable oils. At times, a portion of the softer constituents are hardened. This is particularly true if the vegetable oils which have a tendency to revert in flavor are utilized. The accompanying Table 183 shows analytical data for two typical blended shortenings.

TABLE 183

Properties of Blended Shortenings Made from Meat Fats and Vegetable Oils

Property	Animal-Vegetable[a]	Vegetable-Animal[b]
Free fatty acids, %	0.10	0.10
Smoke point, °F.	400°	400°
Iodine number	75.5	95.5
Color (Lovibond)	20 yellow, 1.2 red	20 yellow, 2.0 red
Stability, Swift A.O.M.	20 hours	25 hours
Flavor	Bland	Bland

[a] Composed of 20% oleostearine, 20% lard, 20% tallow, and 40% cottonseed oil.
[b] Composed of 60% cottonseed oil, 20% soybean oil, 10% oleostearine, and 10% hydrogenated cottonseed oil stearine.

(b) Blended Shortenings from Vegetable Oil. In this type of shortening, saturated glycerides are obtained entirely from hydrogenated vegetable oils, which are usually hydrogenated to an iodine number of 10 to 15 and have melting points of 135° to 145° F. Ten to 15% of the highly hydrogenated fat is mixed with the soft oils to obtain the desired

consistency and plasticity. Again, in this type of product, if revertible vegetable oils, such as soybean oil, are used, they are usually hydrogenated as much as possible to overcome the reversion tendencies. Cottonseed and peanut oils are the preferred ingredients. Table 184 gives analytical data on a typical all-vegetable blended shortening.

TABLE 184

Properties of a Blended Shortening[a] Made from Vegetable Oils

Property	Value
Free fatty acids, %	0.10
Smoke point, °F.	400°
Iodine number	90.2
Color (Lovibond)	20 yellow, 2.0 red
Stability, Swift A.O.M.	30 hours
Flavor	Bland

[a] Composed of 50% cottonseed oil, 40% partially hydrogenated soybean oil, and 10% hydrogenated soybean oil stearine.

2. All-Hydrogenated Shortenings

All-hydrogenated shortenings were introduced in the early part of this century and have gained steadily in popularity, until today about half of all the shortening produced in the United States is of this type. Because of their resistance to rancidity, and their superior creaming properties, plasticity, and uniformity, they are preferred by commercial users, such as bakers, hotel and restaurant chefs, and deep fat fryers. Their increased desirability is reflected by the fact that they usually command a premium in price.

Cottonseed oil has always been the major raw material for this type of shortening, largely because of its greater availability but also because of its good properties. Soybean, peanut, corn, palm, sunflower, and small amounts of coconut oil are commonly employed. The oils may be hydrogenated together or individually to the same or different iodine numbers and blended. Even if only one oil is used, it may be hydrogenated in portions to two or more different iodine numbers. Since the final hydrogenated oils usually have a melting point under 100° F., a small percentage, usually not exceeding 5%, of substantially completely hydrogenated oil is added to raise the melting point and increase the plastic range. If the softer constituent is hydrogenated above a melting point of about 100° F., the product will become too hard for general bakeshop use at the lower temperatures. The object of hydrogenation is to convert as large an amount as possible of the linoleic acid and fatty acids of higher unsaturation to oleic acid, thereby increasing the stability without raising

he melting point above that required for proper consistency. The forma-ion of stearic and iso-oleic acids is held to a minimum. All-hydrogenated hortenings intended for general bakeshop use and prepared from cotton-eed oil usually have a Swift stability of 70 to 100 hours. Table 185 gives nalytical data for a typical all-hydrogenated all-purpose shortening.

TABLE 185

Properties of All-Purpose All-Hydrogenated Shortening

Property	Value
Free fatty acids, %	0.03
Smoke point, °F.	400°
Iodine number	68
Color (Lovibond)	20 yellow, 1.8 red
Stability, Swift A.O.M.	90 hours
Flavor	Bland

D. Utilization of Shortenings

1. Frying Fats

The deep fat frying industry uses large quantities of fats for the frying of potato chips, shoestring potatoes, doughnuts, popcorn, nuts, and fried noodles. The prime requisite of fat used for this purpose is stability. The fats are heated at 325–385° F. for long periods in open metal vessels. The fat which is absorbed by the fried foods is replaced with fresh fat as the process continues. Nevertheless, the heat and metal greatly accelerate oxidation and polymerization. Potatoes, nuts, and fried noodles must remain fresh for considerable periods of time, since they are packaged and subjected to rather long holding periods in their normal channels of distribution. Doughnuts are not usually held for long periods, and stability is not as important a factor in the fat used for frying this type of material as for the other fried foods.

As the stability of the fat decreases, the stability of the fried foods likewise decreases. Table 186 [9] shows the relation of the keeping time of the oil during the frying operation to the stability of the potato chips fried therein, as well as changes in some of the other properties of the fat during frying.

Another requisite of frying fats is a high smoke point, because commercial fryers desire to keep smoke out of their shop. However, this property is overemphasized, for breakdown of the fat during the frying operation quickly causes an increase in free fatty acids with consequent decrease in the smoke point. The more stable the fat is to oxidation and polymerization, the less breakdown there will be.

[9] G. T. Carlin and E. Lannerud, *Oil & Soap,* **18,** 60–62 (1941).

TABLE 186

Effect of Decrease in Keeping Quality of Hydrogenated Vegetable Oil on Keeping Quality of Potato Chips Fried Therein[a]

Time of heating of fat, hours	FFA, %	Smoke Point, °F.	A.O.M., hours	Initial peroxide value	Days before potato chips turned rancid at 145°F.
0	0.03	425	118	0.0	96
27	0.15	380	4	4.2	6
38	0.22	360	3	6.0	4
45	0.27	380	2	4.0	6
70	0.41	350	4	5.2	3
91	0.79	320	5	3.0	4
113	1.01	340	8	2.2	5

[a] From G. T. Carlin and E. Lannerud, *Oil & Soap*, **18**, 61 (1941).

Frying fats also must have resistance to foaming. As the heating continues for long periods, the fats tend to foam when the moist foods are placed in them. Foaming has been correlated with decrease in refractive index and iodine number.[10] The hydrogenated oils have greater resistance to foaming than the blended shortenings.

An extended plastic range is not required in frying fats, since they are used in the melted form. However, the melting point must be below a definite limit to prevent the solidification of the fat on the surface of the fried goods after they have cooled to room temperature, which gives them an undesirable appearance and a waxy surface.

The obvious means of producing a fat of high stability for such purposes is hydrogenation. Cottonseed, peanut, and sesame oils are preferred as starting materials, since they do not revert in flavor and impart objectionable odors and flavors to the fried goods. Conditions of hydrogenation are controlled so as to reduce the highly unsaturated acids as much as possible, and hydrogenation is allowed to proceed until the maximum tolerable melting point is reached. This is usually 100° to 105° F. Since, as pointed out above, doughnuts are not necessarily fried in extremely stable fats, blended shortenings have been shown to be quite satisfactory for this purpose.

2. Biscuit and Cracker Shortenings

Shortenings to be used in biscuits and crackers also must have long keeping qualities, since these products are usually packaged and held for considerable periods of time before consumption. Such baked goods are almost entirely prepared in large factories where raw materials are stored

[10] H. E. Robinson, H. C. Black, and H. S. Mitchell, *Oil & Soap*, **17**, 208–210 (1940).

and the doughs prepared under controlled conditions of temperature and humidity. The chief function of the fat in this type of product is to produce a shortening effect. Good creaming qualities are not required and plastic range is not an important consideration.

The preferred biscuit and cracker shortenings are the all-hydrogenated vegetable oils, hydrogenated under conditions to give maximum stability consistent with ability of the shortening to be mixed easily with the dough. The products usually melt at about 100° F. and have stabilities of 150 to 200 hours by the Swift method. The reversion-resisting oils, such as cottonseed oil, are preferred as raw materials. However, due to the competitive nature of this type of baking business, large quantities of the meat fats—lard and oleo oil—find their way into biscuit and crackers. These meat fats generally are lower in price than the all-hydrogenated shortenings.

This type of fat is used in the preparation of prepared biscuit, muffin, and pancake mixes, which have greatly increased in popularity during the last few years. The addition of liquids to the mixture is all that is necessary to make the dough or batter ready for use.

3. Emulsifying-Type Shortening

About 1933, a special type of shortening, particularly intended for use in cakes, appeared on the market. This product was new, although similar products have been known for many years.[11] It consisted of an all-hydrogenated shortening (containing mono- and diglycerides) prepared separately by heating a portion of the fat with an excess of glycerin in the presence of an alkaline catalyst, and adding the product to the main body of the shortening. The result is a shortening which contains an amount of combined glycerin in excess of that required for triglycerides. The mono- and diglycerides have a marked surface activity due to the presence of free hydroxyl groups. Their use results in a greater dispersion of the shortening in batters. The outstanding characteristic of such batters is that a greater proportion of sugar and moisture in relation to the flour can be used than when the emulsifying agent is not added. The cakes produced are also finer in texture, more moist, and have a better keeping quality. This allows the commercial baker to produce cakes which will remain fresh for longer periods of time. The terms "high ratio" and "superglycerinated" have been applied to this type of shortening.[12] About one-fourth of the all-hydrogenated shortenings generally produced are of this type.

The main portion of the emulsifying-type shortenings is used in cakes. The appearance, consistency, and stability of these shortenings are quite

[11] C. Ellis, U.S. Pat. 1,261,911 (1918).
[12] The term "high-ratio" is copyrighted by Procter & Gamble Co.

similar to those of the ordinary all-hydrogenated shortenings. However, the free fatty acid content is higher and the smoke point is lower. This does not affect the performance in cake making.

The manufacture of monoglycerides, as well as shortenings containing them and baked goods made therefrom, are covered by patents.[13] Other products made by combining polyhydric alcohols other than glycerin with fatty acids have been patented and can be used.[14] However, monoglycerides and diglycerides continue to be the preferred emulsifying agents. Many other materials have been tested for their emulsifying action, but none thus far known is as effective as the partial esters of polyhydric alcohols. Soybean lecithin will function to a certain extent but not as satisfactorily as the polyhydric compounds.

4. Confectioners' Fats

In the past, cocoa butter and coconut and palm kernel oils have been used almost exclusively in the candy and confection trade. These oils have specific properties which give them special utility in the various applications in this industry. Their outstanding properties are low, but quite sharp melting points—and a high resistance to oxidation. Because these oils have been available at prices which were generally somewhat lower than those of domestic oils and fats, little work was done in an attempt to reproduce the properties of these oils in products made from domestic raw materials. However, cessation of the importation of coconut and palm kernel oils into this country when the South Pacific was occupied by Japan in 1942 necessitated the development of fats for this industry from domestic sources.

Blends of oleo oil and hydrogenated vegetable oil, as well as hydrogenated vegetable oil alone, were developed for use in the candy industry. The requirements are good flavor and keeping quality and proper consistency. Filler fats, the fats used for the manufacture of cream icings, require the proper relationship between creaming quality, melting point, and viscosity. The latter is important, since fillers are applied in automatic machines. Hydrogenated vegetable oils, particularly cottonseed and peanut oil, give very satisfactory results. The addition of several tenths of one per cent of lecithin reduces the apparent viscosity to the desired point.

The production of a satisfactory coating fat for use in coating candies and cookies is more difficult. High melting points, without gumming tendencies, are required. However, satisfactory products have been made

[13] H. S. Coith, A. S. Richardson, and V. M. Votaw (to Procter & Gamble Co.), U.S. Pats. 2,132,397 (1938) and 2,132,398 (1938). H. C. Black (to Industrial Patents Corp.), U.S. Pat. 2,320,844 (1943).

[14] M. C. Reynolds, B. J. Harris, and A. K. Epstein (to Procter & Gamble Co.), U.S. Pat. 2,132,436 (1938).

by the hydrogenation of vegetable oils. Peanut oil is the best raw material, but cottonseed oil has been used very satisfactorily.

In some cases, the substitutes which were developed for cocoa butter and coconut oil are superior to the original material. An example is a coating for ice cream bars. The material developed, which is manufactured from hydrogenated vegetable oils, is not as hard and brittle as that produced from coconut oil. The latter tends to shatter into pieces when eaten, while the product made from hydrogenated cottonseed oil is more plastic, even after being frozen.

E. Effect of Shortening in Baked Goods

It is impossible here to delve deeply into the action of shortening in baked goods. Nevertheless, the discussion of some of the rudiments of the behavior of shortening is appropriate, since a large part of shortening and other plastic fats is consumed in the manufacture of baked goods. Pie crust contains 35 to 50% of fat; pound cakes, 15 to 30%; doughnuts, 15 to 20%; cookies, 5 to 20%; white and yellow layer cakes, 12 to 15%; crackers, 8 to 12%; and bread, about 3%.

In baked goods fats are chiefly important because of the role they play in the development of physical structure. They also contribute somewhat to flavor but this is of secondary importance. Within limits, the various types of shortening may be substituted in the different classes of baked goods in household baking. However, in the competitive commercial baking field, where all ingredients are carefully controlled and manufacturing is carried out under exacting conditions, differences in fat show up markedly, and the proper type is required for each product. Uniformity within the various classes of shortening is necessary, since the bakers desire to produce products of uniform quality.

Fats have two chief functions in baked goods. These are their leavening or creaming action and their lubricating function.

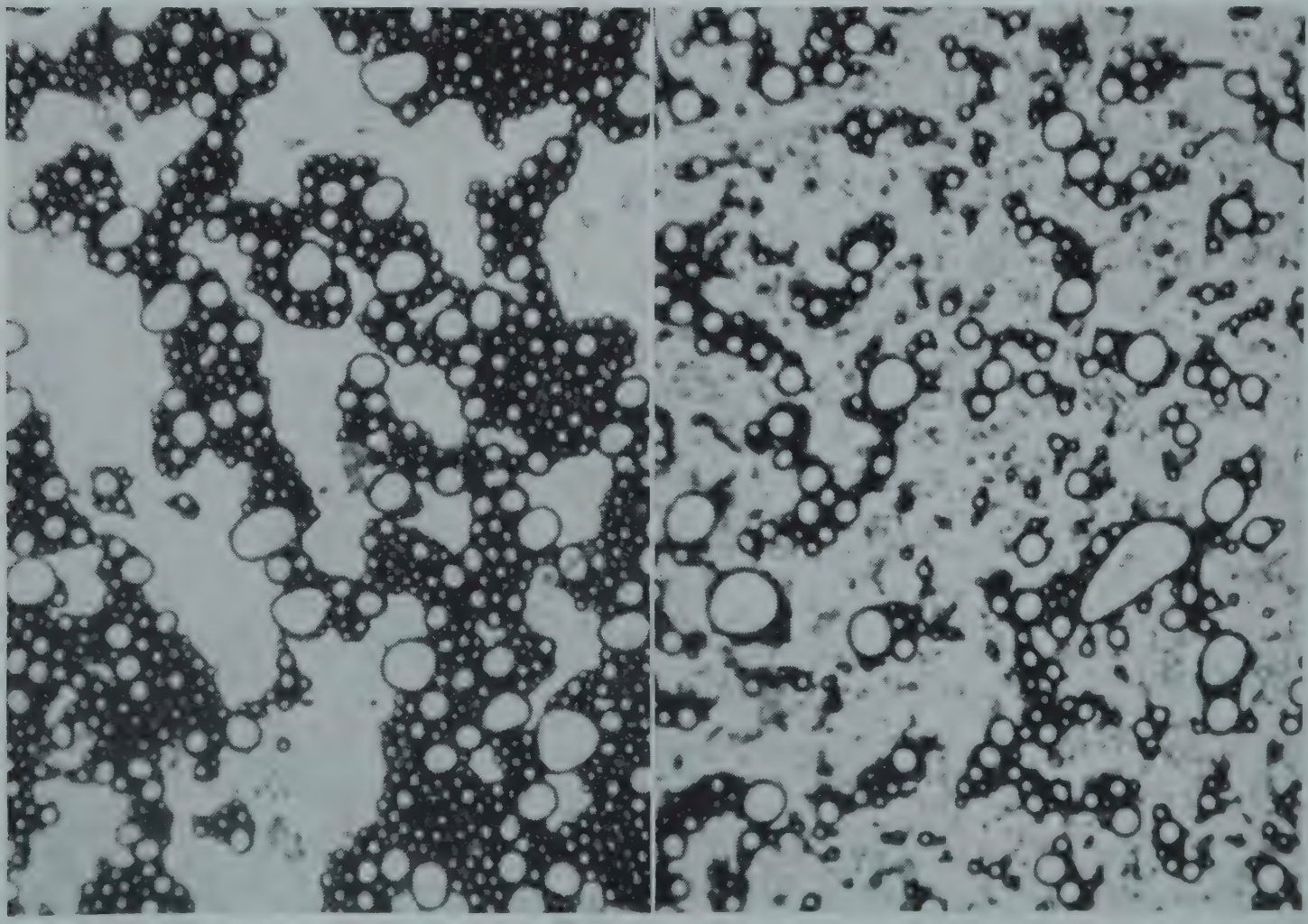
1. Leavening or Creaming Action

Baked goods may be divided into two broad classes on the basis of the leavening process: (*a*) those which are leavened with yeast, and (*b*) those which are leavened by other means. In certain yeast-raised goods, a satisfactory cell structure may be produced without the use of fat, although fat is considered an aid by the modern bread baker. Other types of baked goods require a considerable proportion of fat for the development of the characteristic cellular structure.

Cake batters consist of dry ingredients—flour, sugar, salt, baking powder and fat—mixed with more liquid ingredients, such as milk and eggs. The dough is a three-phase system consisting of: (*a*) fat, (*b*) other ingredients, and (*c*) air. Careful microscopic examination of a batter in

which the fat has been incorporated reveals that in each particle of fat there are enclosed small bubbles of air. This incorporation of air into the fat is called creaming, and the more air that is dispersed in the fat within the batter, the better is said to be the creaming quality. There is a close correlation between the volume and texture of the finished baked goods and the amount of air, as well as the degree of dispersion of the fat and of the air within the fat. When a batter is baked, the plastic fat melts and the air particles are released from it. The increase in volume in baking is due in some degree to the expansion of the air within the air cell, but a much greater proportion is caused by the expansion of water vapor and carbon dioxide from baking powder. It has been shown by photomicrographs that just before the baking operation is completed there is rapid motion of the air particles within the batter. As the temperature reaches the point where the starch and protein of the flour coagulate, the final structure of the cake is fixed. If there were many small air bubbles, the cells will be greater in number and thus smaller than if there were relatively few bubbles—and the texture of the cake will likely be finer.

If an emulsifying agent is used in the shortening, the fat is dispersed in smaller particles and the air is more finely dispersed within the fat, as



(a) (b)

Fig. 192. Photomicrographs (×37) of white layer cake batters made with (a) standard all-hydrogenated vegetable oil shortening and (b) superglycerinated all-hydrogenated vegetable shortening (containing 5% of a mixture of mono- and diglycerides).

illustrated in Figure 192. In such batters, it is possible to use a higher percentage of sugar and water and still have a fine-textured cake.

2. Lubricating Function of Shortening

Examination under the microscope of the finished cake will reveal that the gluten and starch structure is interspersed with films of fat. These cause the product to be tender and easily broken. Pastries are formed from stiff doughs which are rolled into a thin sheet without excessive prior mixing. The fat is incorporated into the dough by this means in thin layers. After baking, the pastry breaks easily along these lines in which the fat was distributed. Fats vary somewhat in their ability to produce tender, flaky pastries. Liquid oils will not function at all, since they tend to collect in the dough in droplets rather than being dispersed in streaks or films.

F. Dry Shortening

In recent years, a new type of so-called shortening has appeared on the market. It has the appearance of powdered skim milk. However, it contains about 80% fat and is prepared by emulsifying either shortening or cooking oil in skim milk and spray-drying the mixture.[15] The final product contains 75–80% fat and 20–25% dry skim milk solids. Other products have been described in which carbohydrates[16] and dried whey[17] are incorporated.

The chief use of such material appears to be in dry mixes which are intended for use in baked goods containing a small percentage of fat, such as doughnuts, biscuits, etc. The advantages claimed for dry shortenings are as follows: (*a*) improved stability as compared to ordinary shortenings; (*b*) greater ease in mixing with other ingredients; and (*c*) lower packaging costs. The disadvantages are: (*a*) lack of creaming power; (*b*) lack of shortening value; and (*c*) limited flexibility in formulations.

III. Salad and Cooking Oils. Salad Dressings

In contrast to the shortenings which are solid at room temperature, salad and cooking oils are liquid. Furthermore, salad oils will remain liquid at 40° F. and produce mayonnaise emulsions stable at much lower temperatures. The difference in chemical makeup of the cooking and salad oils as contrasted to the shortenings is, of course, in the smaller proportion of highly saturated glycerides in the former. Salad oils, which remain liquid at lower temperatures than cooking oils, contain a smaller proportion of saturated glycerides than the latter.

While plastic shortenings are generally preferred in the United States, it should be emphasized that liquid oils are used for all forms of cooking

[15] E. J. Fechner (to Page Milk Co.), U.S. Pat. 2,065,675 (1936).
[16] G. H. Kraft (to Kraft-Phenix Cheese Corp.), U.S. Pat. 2,035,899 (1936).
[17] W. A. Heyman (to Granular Foods, Inc.), U.S. Pat. 2,332,513 (1943).

and baking in some other countries, as well as in certain localities of this country. They are used to some extent by commercial deep fat fryers where high stability is not a prerequisite, *e.g.*, for doughnuts. They are used also in the packaging of canned meats and fish, such as sausages and sardines. Salad oils, which will be described later, are used for making mayonnaise and salad dressings.

A. Cooking Oils

Cottonseed and peanut oils are the preferred raw material for the manufacture of cooking oils. The crude oils are refined in much the same manner as for the manufacture of shortening. Generally, light colors are not required in the oils, and unless the refined oils are very dark, the bleaching operation is omitted. The oils are deodorized in order to remove all traces of odor and flavor and are then packaged in drums, or in smaller containers of from one-pint to five-gallon capacity. Metal containers are the preferred type of package since they exclude light which accelerates flavor deterioration. Also, such packages are easily made air-tight, so that oxygen may be excluded.

B. Salad Oils

Salad oils are manufactured from cottonseed oil by refining and then winterizing. The latter operation is usually carried out by placing the refined oil in tanks, where it is slowly chilled by means of cold air or by circulation of a refrigerant around or through the tank. As the temperature drops, the glycerides containing the more saturated acids slowly crystallize and separate. When the temperature has been reduced to 40–45° F., the partially solidified mass is passed through filter presses which strain out the solid glycerides leaving the softer more liquid oil, commonly referred to as "winter" oil. Salad oils are usually not bleached, since the trade is accustomed to and usually demands darker colored oils. The Lovibond color reading on salad oils is usually in the range of 4.0 to 7.0 red, as compared to 1.5 to 2.5 red for shortening. Salad oils are thoroughly deodorized and packaged in much the same manner as cooking oils. Large manufacturers of salad dressings and mayonnaise purchase their oil in tank car quantities.

One of the most important analytical characteristics of a salad oil is its cold test. This is a measure of the degree of removal of saturated glycerides which crystallize when the oil is held at lower temperatures. When crystallization occurs, the mayonnaise and salad dressing emulsion made from the oil breaks with consequent separation of ingredients. The cold test is determined by placing a four-ounce bottle of the oil in an ice bath and noting the time before crystallization occurs. The standard for the trade is 5½ hours. However, much of the oil on the market holds up

ten to fifteen hours. Recently, considerably longer cold tests have been obtained by the use of crystallization inhibitors.[18] These oils produce salad dressings and mayonnaise which withstand cold temperatures to a better degree than do oils with a shorter cold test.

C. Salad Dressings

1. Mayonnaise

The Food and Drug Administration has adopted an official standard or definition for mayonnaise. This standard is as follows:

> The semisolid emulsion of edible vegetable oil, egg yolk or whole egg, a vinegar and/or lemon juice, with one or more of the following: salt, other seasoning commonly used in this preparation, sugar and/or dextrose. The finished product contains not less than 50% of edible vegetable oil.

Actually, the oil content usually ranges between 70 and 80%. Table 187 shows typical formulas for two types of mayonnaise.

TABLE 187

Typical Formulas for Mayonnaise

Ingredient	Light body		Heavy body	
	Pounds	Ounces	Pounds	Ounces
Egg yolk	8	0	10	0
Mustard flour	0	8	0	8
White pepper	0	¼	0	¼
Salt	2	0	1	13
Sugar	1	8	1	0
Vinegar	9	0	7	8
Salad oil	74	0	78	0
Water	5	0	1	3
Total	100	¼	100	¼

In its physical makeup, mayonnaise constitutes the type of emulsion in which droplets of oil are dispersed throughout an aqueous or waterlike material. An emulsion of the mayonnaise type is composed of three parts: (*a*) the continuous phase comprising the aqueous or waterlike material (vinegar and the natural moisture in the eggs); (*b*) the dispersed phase consisting of the droplets of oil; and (*c*) the emulsifying agent, which is the egg solids. An examination of a thin film of mayonnaise with a microscope shows small droplets of oil dispersed in the aqueous material.

[18] E. W. Eckey and E. S. Lutton (to Procter & Gamble Co.), U.S. Pat. 2,266,591 (1941).

Around each oil droplet is the emulsifying agent. The emulsifying agent not only causes the oil to split up into small particles, but also adheres to the outer surface of each particle, forming a practically complete protective coating. This coating prevents the oil droplets from running together and, hence preserves the emulsion and prevents separation.

In practice, the emulsion is made by placing the eggs and the dry ingredients in a bowl, along with a portion of the vinegar. A mechanical mixer is started and the oil is gradually beat in. Finally the thick emulsion is thinned out by adding the remainder of the vinegar. There are also continuous methods of making the emulsion which employ the colloid mill or other types of homogenizer. Better results are obtained if the ingredients are cooled somewhat prior to their mixing.

2. Other Salad Dressings

Probably the most common of other salad dressings is the type which is similar in appearance to mayonnaise but contains less oil. The stiff body is obtained by the addition of a cooked starch. Other ingredients are eggs, vinegar, and spices.

In addition to these salad dressings, many others appear on the market. One of these is French dressing, which is generally a mixture of salad oil with flavoring agents, such as vinegar, sugar, salt, and spices.

IV. Margarine

A. Definition

Margarine is an emulsion of edible plastic fats with cream, milk, or skim milk, with or without added emulsifying agents, sodium benzoate, certified coloring materials, flavors, and vitamins.

B. History

Like many important and useful products, margarine resulted directly from wartime research, stimulated by shortages. During the Franco-Prussian War, a serious shortage of edible fats occurred in France, and Napoleon III offered a prize to the inventor who would create a "palatable, appetizing, nutritious, and economical alternate" for butter.[19] In 1870, the French chemist, Mége-Mouriés, won the prize by producing the first margarine. By 1872 production had grown to commercial importance in France, and it was soon being produced in other places, including the United States.

The first margarine was made by blending the lower melting fractions of low temperature rendered beef fat with water, bicarbonate of soda,

[19] K. Snodgrass, *Margarine as a Butter Substitute*, Stanford Univ. Press, Stanford Univ., Calif., 1930.

casein from milk, and mammary tissues. The mixture was agitated and chilled to a semisolid state. The use of mammary extract, which the inventor intended to cause a conversion of the beef fat to milk fat, was soon abandoned, as such conversion was, of course, impossible. It was soon found that, if the milk were allowed to ripen, the production of butterlike flavors resulted. The physical properties of margarine were improved by quick chilling of the emulsion of ripened milk and fat by allowing the emulsion to flow into a vat of cold water. This resulted in solidification of the product in small crystals. The chilled mass was then worked, to give it a smooth consistency and to regulate the moisture content. Later, the emulsion was chilled by spraying it with cold water. Only recently have chill rolls and Votators been used for chilling the emulsion.

C. Margarine Legislation

Both federal and state legislation intended to control margarine have restricted its manufacture and distribution. The first federal law on margarine was enacted in 1886. It decreed that margarine must be clearly labeled "oleomargarine." At that time, beef fat was used exclusively—hence the prefix "oleo," which refers to beef fat. Today, the larger part of the product is made from purely vegetable oils, but the term "oleomargarine" must still be used.

The present federal taxes amount to ¼ cent per pound for uncolored margarine and 10 cents per pound for colored margarine. The states have taxes ranging up to 15 cents per pound and up to $400.00 for retail dealer licenses. Federal licenses amount to $600.00 for manufacturers, $480.00 for wholesalers of colored margarine, $200.00 for wholesalers of uncolored margarine, $48.00 for retailers of colored margarine, and $6.00 for retailers of uncolored margarine. The federal courts have held that all margarine must be nearly white. If it has a noticeably yellow hue, due either to the natural colors of the ingredients or added dyes, it must be sold as colored margarine. The result is that nearly all margarine is sold uncolored, and individuals must color their own purchases with the packet of coloring material which, as a rule, is supplied with the print by the manufacturer of the product.

An act of Congress has established the legal definition of margarine. It is very broad, including any plastic fat containing in excess of 1% moisture. The only exception is that of puff paste shortening, which must have a melting point over 118° F. Also, the Federal Food, Drug and Cosmetic Act provides for a definition for margarine. The Federal Security Administration established a standard of identity for the product in 1941. This states what materials may be used and excludes all other ingredients. It also definitely specifies what information the label of the product must include.

D. Production and Consumption

The accompanying table (Table 188) shows the total production of margarine in the United States for the fiscal years 1931 to 1945. The out-

TABLE 188

Production of Margarine in the United States, 1931–1945[a]

Fiscal years, ending June 30	Production, 1000 pounds	Fiscal years, ending June 30	Production, 1000 pounds	Fiscal years, ending June 30	Production, 1000 pounds
1931	277,773	1936	371,738	1941	341,852
1932	215,342	1937	389,264	1942	357,805
1933	219,043	1938	415,404	1943	437,268
1934	243,187	1939	332,973	1944	486,026
1935	353,821	1940	303,717	1945	561,561

[a] From *Annual Reports of the Commissioner of Internal Revenue*, Washington, D. C.

standing feature of this tabulation is the large increase in production in the years 1942 to the present. This was occasioned by the scarcity of butter and other fats and oils.

E. Margarine Ingredients

1. Oils

We have seen that oleo oil was the fat originally employed in the manufacture of margarine. Later, oleo oil was supplemented with neutral lard, and these two fats were those principally used for many years. Vegetable oils were too soft for the purpose, and refining and deodorization techniques were inadequate to produce the necessary light colors and neutral flavors. As refining and deodorization improved, the lauric acid oils, coconut and palm kernel, were utilized; these, when mixed with oleo oil or oleo stock and liquid vegetable oils, gave products of satisfactory consistency. In 1934, a federal processing tax was imposed on coconut and other foreign oils and thereafter the usage of these oils decreased.

Up until this time, hydrogenated domestic vegetable oils, *e.g.*, cottonseed and soybean, had been used to some extent in combination with other oils but not as the sole ingredient. Hydrogenation processes were continually improved, as were margarine manufacturing methods, and products made from all-hydrogenated vegetable oils or blends of hydrogenated vegetable oils with unhydrogenated oils were developed. Similar refining and processing of lard and other meat fats now permits the manufacture of good-quality margarine containing appreciable quantities of these fats.

At present, some manufacturers prefer the use of an all-hydrogenated oil alone, while others use a blend of hydrogenated oils with unhydrogenated oil. If hydrogenated cottonseed or soybean oil is employed, it is hydrogenated to a Wiley melting point of 96° to 98° F. If a blend of hydro-

genated and unhydrogenated oil is used, the hydrogenated portion is usually of 101° to 105° F. melting point. Sixty to 80% of such oil is blended with 20% to 40% of unhydrogenated oil.

Table 189 shows the amount of the various fats and oils used in the manufacture of margarine for some of the years since 1917. The increase

TABLE 189

Fats and Oils Used in the Manufacture of Margarine in the United States, 1917–1945[a]

Oil or fat	Amount used, million pounds						
	1917[b]	1922[b]	1927	1932	1937	1942	1945
Oleo oil	96.7	41.0	49.5	12.5	12.3	22.5	11.9
Lard	42.4	27.1	25.0	9.4	1.8	8.1	9.7
Oleostearine	2.5	4.6	5.4	3.7	3.4	2.9	5.6
Other meat fats	—	3.1	4.6	0.5	1.3	4.1	0.1
Coconut oil	19.8	57.4	122.6	123.2	73.8	3.5	—
Palm kernel oil	—	—	—	—	7.9	—	—
Babassu oil	—	—	—	—	14.6	0.3	—
Cottonseed oil	63.7	15.4	24.6	15.1	173.6	166.4	215.0
Soybean oil	—	—	—	—	31.8	133.3	211.1
Peanut oil	10.5	11.6	4.7	2.5	2.9	0.9	12.3
Other vegetable oils	0.8	0.0	0.8	0.3	2.8	5.0	12.7

[a] From A. E. Bailey, *Industrial Oil and Fat Products*, Interscience, New York, 1945, p. 263; and *The Fats and Oils Situation*, Bureau of Agricultural Economics, April, 1945.

[b] Fiscal years, beginning July 1; data for other years are calendar years.

and decline in use of coconut oil, the decrease in oleo oil and lard utilization, and the increase in the use of domestic vegetable oils are the outstanding features of these data. It is to be noted that, at the present time, cottonseed oil supplies nearly half of the oil used.

In the hydrogenation of the oil, an attempt is made to obtain three principal characteristics. The first of these is the so-called "get-away." This refers to the melting characteristics of the fat. It is desired that the fat melt quickly in the mouth and not be waxy or gummy. The second characteristic is plastic range, so that margarine made from the oils will be workable and easily spread when held at ice box temperatures, and not be too soft when allowed to stand at room temperature in hot weather. The third characteristic is stability. Although oxidation is not an important factor in the deterioration of margarine, an attempt is made to reduce the linoleic acid and acids of higher unsaturation to as small a proportion as possible in order to minimize the effect of oxidation on the fat.

The principal physical properties used for controlling the hydrogenation and formulation of oils for margarine are the set point and the melting point. Usually the Wiley melting point is employed. As narrow a range as possible between the set point and the Wiley melting point is

usually desired. It has been claimed that high percentages of iso-oleic acid are desirable.[20]

Deodorization is very important in the processing of oils intended for use in margarine. Any oil flavor is objectionable, because it interferes with the flavor contributed by the milk. The original flavor of the fat must be entirely bland and, for the highest quality margarine, only those oils which do not revert are entirely satisfactory. For this reason, cottonseed and peanut oils are specified in preference to the oils which have a tendency to revert in odor and flavor.

2. Milk

Next to oil, from a quantitative standpoint, the most important ingredient entering into the composition of margarine is milk or skim milk—in modern margarine it supplies the flavor. In the early days of the industry, milk was allowed to ripen with the natural bacteria originally present. This led to nonuniform and, many times, undesirable flavors. Today, good quality milk or skim milk is pasteurized and inoculated with carefully selected and properly propagated bacterial cultures of the lactic acid-producing and other types. These cultures which produce the flavor material are identical with the cultures employed in ripening cream for butter manufacture. The reactions that take place are apparently quite similar; the cultures in either case produce diacetyl and acetylmethylcarbinol, among other compounds.

In the preparation of the milk or skim milk for margarine manufacture, the growth of the culture is carefully controlled by maintaining the milk at the desired temperature and allowing the reaction to proceed until it has reached the desired point, as determined by acidity formation. When the reaction has reached the proper point, the milk is cooled below the temperature of rapid bacterial growth. It is then ready for use in making the emulsion.

In addition to the flavor-bearing materials produced by the action of cultures on the milk or skim milk used in the margarine, flavor concentrates distilled from cultured milk are sometimes used.

3. Other Ingredients

Since a large proportion of the margarine produced is used as a spread for bread, and for its flavor in cooking and baking, 2.5 to 3.5% of salt is added. Fine-grained salt, which is easily dissolved, is usually specified.

In order for the emulsion of fat and milk to remain stable, emulsifying agents must be added to aid dispersion of the fat and prevent "leaking" of moisture. The most common emulsifiers are monoglycerides, chiefly mono-

[20] H. W. Vahlteich, C. H. Haurand, and R. H. Neal (to Best Foods, Inc.), U.S. Pat. 2,047,530 (1936).

stearin, used at a level of a few tenths of one per cent. Other derivatives of glycerin, such as sodium sulfoacetate derivatives of mono- and diglycerides are also used. Lecithin is also commonly employed to improve the performance of margarine in frying. This phospholipid prevents excessive spattering and adhering of milk solids to the frying pan.

In the last few years, margarine has been fortified with vitamin A to further add to its excellent nutritional quality. According to the United States Food and Drug Standards, fortification is optional, but if margarine is fortified, at least 9,000 units per pound must be added. It is estimated that 99% of all margarine sold to civilians in 1944 was fortified with vitamin A.[21] Probably, the percentage is higher than that at the present time. Recently, several large manufacturers have increased the amount of vitamin A to 15,000 units per pound.

The source of vitamin A is fish and marine animal liver oils. Some of these are high in potency, ranging from 100,000 to 200,000 units per gram, and may be used as such directly. Other oils of comparatively low potency (15,000 to 50,000 units per gram) are used as raw materials for concentration techniques, such as molecular distillation, saponification, or solvent concentration, and potencies of over 1,000,000 units per gram are available today.

Since the oils are of fish origin and the processing does not completely eliminate fishy odors and flavors, margarine manufacturers prefer to use the oils that furnish the required potency but, at the same time, impart the least possible objectionable odor and flavor to the finished margarine.

Another factor affecting the selection of concentrates is the stability of the vitamin. Since manufacturers are subject to having samples picked up by the Food and Drug Administration for analysis at any time, the minimum guarantee of 9,000 or 15,000 units per pound on the package must always be present. There is slight loss of vitamin A potency as the product ages, and an excess is always added to allow for destruction and for variation in assay methods. At present, concentrates are available which impart undetectable amounts of flavor, even when added in quantities sufficient to supply 18,000 to 20,000 units. Also, the concentrates do not lose potency over long holding periods. Manufacturers have adequate control systems, based on spectrographic methods, to insure the incorporation of the desired amounts of vitamin A to each batch of product. Most of the concentrates contain small amounts of vitamin D, which of course enters also into the margarine.

F. Manufacturing Methods

After the fats have been properly deodorized and the skim milk ripened, they are weighed out in the desired proportion. Emulsions are then made,

[21] Council on Foods and Nutrition, *J. Am. Med. Assoc.* **126,** 168 (1944).

either by the batch system in a vat equipped with agitators and temperature controls, or sometimes continuously by proportioning the fats and aqueous materials directly into a votator chilling unit where emulsification, as well as chilling, is obtained. In either case, the result is the formation of a water-in-oil emulsion. If emulsifying agents are employed, they, along with the salt and vitamin concentrates, are added.

If the chill roll is used, the flakes are removed from the roll, passed through a machine which "works" them by kneading or agitation and extrusion, and the mass is placed in trucks and allowed to temper. As in shortening manufacture, certain crystal changes take place which improve the consistency and plastic range of the product. After the tempering period, the margarine is placed in machines which further work it by mechanical agitation. It is then formed into prints and wrapped and packaged in individual cartons.

If the Votator method is used, the emulsion is either formed therein continuously as previously mentioned or is preformed and pumped through the Votator. From the Votator, the product goes directly to the printing machine or is given a tempering period similar to that of the roll-chilled product.

Considerable care is exercised in the packaging operation to avoid contamination of the product. Parchment paper is usually used, and the prints after wrapping are placed in waxed cartons which are folded and closed mechanically. A small packet of oil-soluble dye sufficient for coloring the margarine is inserted inside or attached to the waxed carton.

G. Physical Properties

There are two main physical properties of margarine which govern the formulation and manufacturing procedures. The first of these is "get-away" or the ability of the fat to melt quickly in the mouth with the release of the flavor-bearing milk. If the melting point is too high or the emulsion improperly made, or if the margarine has not been properly handled in the chilling or tempering processes, the final product will not melt in the mouth as quickly as desired.

The second characteristic is plastic range. This is one of the superior characteristics of margarine. If the oils used have the proper physical properties, and if the emulsion is properly made and tempered, the product is spreadable as taken directly from the ice box. Also, in extremely hot weather, it will not melt or become unduly soft and oily.

H. Pastry Margarines

1. Danish Pastry Margarine

This type of margarine is intended for use in the class of baked goods known as Danish pastry. It is prepared from fats of higher melting point

than those used in table margarine, since melting in the mouth is not a requirement for the Danish pastry margarine. Cottonseed oil, oleo oil, and oleostearine are the common fat ingredients. The emulsion is made and chilled in much the same manner as the ordinary margarine emulsion.

2. Puff Paste

This product is not a margarine according to the present legal definition, since it is churned with water instead of milk. It is used in the manufacture of puff pastry by the baking industry. It usually contains low percentages of moisture and is produced to have a very waxy texture. Since puff pastry derives its flaky, tender characteristics from the alternate layers of dough and fat obtained by rolling, it is necessary that the fat used have unusual waxy, cohesive properties in order that extremely thin sheets may be rolled out without rupture. The fats usually employed are oleostearine and vegetable oil, with sufficient amounts of the former to produce the desired waxiness.

I. Deterioration

Margarine, like butter, is a perishable product and, in general, undergoes the same type of deterioration. Rancidity is not an important factor, since extensive oxidation is not likely to occur. However, flavor reversion of any of the oils is an important consideration. If the oils revert in flavor, the butterlike flavors of the milk are masked.

Margarine is usually held under refrigeration. This minimizes bacterial and mold action and, at the same time, prevents loss of the volatile odor and flavor-producing materials. Much of the flatness in flavor of old margarine, provided it is made from good quality oil, is probably due to volatilization of the diacetyl, acetylmethylcarbinol, and other flavoring materials.

V. Miscellaneous Edible Products

Cottonseed lecithin, that is, the dried and bleached phosphatides of cottonseed oil, have been prepared and marketed in a small way, but the darker color and stronger odor of this product as compared with soybean lecithin has retarded its utilization.

The demand for tocopherols for medicinal use as vitamin E, and as an edible antioxidant has stimulated a search for all possible sources of this material. It has been found that hot-well skimmings, produced when cottonseed and other vegetable oils are deodorized under high vacuum and temperature, contain enough tocopherols so that they can be profitably concentrated by molecular distillation.

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CHAPTER XIX

NUTRITION ASPECTS OF COTTONSEED OIL UTILIZATION

The Role of Fat in Human Nutrition

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I. Introduction

Fat may serve many functions in human, as well as in animal nutrition. First of all, it is the foodstuff which possesses the highest caloric value per unit weight, and from this standpoint must be considered the most concentrated food material. As a source of energy under normal conditions, it yields 9.3 kcal. per g., whereas the figure usually assigned as the net heat value of carbohydrate and protein is 4.1 kcal. per g. Moreover, since fat is hydrophobic, it is frequently found in foods in a practically pure form. Carbohydrates and proteins, which are hydrophilic, are usually associated with varying proportions of water in vegetable, as well as in animal products. This results in a far greater variation in the net caloric value of these foodstuffs as they occur naturally than the 2.3:1 ratio which exists between the caloric value of *purified* fats on the one hand and purified carbohydrates or proteins on the other hand. It thus becomes evident that fat is the foodstuff to be employed in greater abundance when the bulk of the diet must be restricted.

In addition to their caloric function, fats serve as the only source of the unsaturated (or essential) fatty acids required for the structural development of animal tissues. They also are of especial importance as carriers of the fat-soluble vitamins. Finally, they are necessary in making diets palatable. Low-fat diets are usually unappetizing, and their use is often associated with a voluntary reduction in caloric intake. During World War I, according to Starling,[1] the civilian population of Great Britain lost weight as a result of failure to consume sufficient of the high-carbohydrate diet which resulted from the wartime fat shortage. In addi-

[1] E. H. Starling, *Brit. Med. J.*, **2**, 105–107 (1918).

tion to the role of fat in rendering foods more palatable, every housewife knows that it is an essential adjunct in the preparation of many baked dishes.

The present chapter will attempt to assess how satisfactorily the various fats, particularly the vegetable ones, can satisfy the various functions enumerated above. A number of reviews have appeared recently on various aspects of fat metabolism, including the nature of deposited fat (Anderson and Williams [2]), the factors related to absorption (Frazer [3, 3a]), and to fat transport (Bloor [4]), the noncaloric functions of dietary fats (Burr and Barnes [5]), the essential fatty acids (Burr [6]), and most recently, the relative nutritive values of animal and vegetable fats (Cowgill [7]). The more general aspects have been reviewed by Burr and Barnes,[8] Barnes and MacKay,[9] Piskur,[10] and Longenecker.[11] A review of the interrelation of carbohydrate and fat metabolism has been published by Deuel and Morehouse.[12] Several excellent compilations of the composition of fats which have appeared recently are those of Hilditch,[13] Jamieson,[14] Bailey,[15] and Markley.[15a]

II. Composition of Fats and Oils as Related to Their Nutritive Value

A. Fatty Acid Composition

Most fats and oils have a relatively similar composition, being composed principally of varying mixtures of triglycerides of palmitic, stearic, and oleic acids. In general, those fats which are liquid at ordinary temperatures have large proportions of oleic acid, while those fats having high melting points contain more of the glycerides high in palmitic and stearic acids. However, since glycerides of these three acids can be synthesized in the animal body from nonfat precursors, their presence in the in-

[2] W. E. Anderson and H. H. Williams, *Physiol. Revs.*, **17,** 335–372 (1937).
[3] A. C. Frazer, *Physiol. Revs.*, **20,** 561–581 (1940).
[3a] A. C. Frazer, *Physiol. Revs,* **26,** 103–119 (1946).
[4] W. R. Bloor, *Physiol. Revs.*, **19,** 557–577 (1939).
[5] G. O. Burr and R. H. Barnes, *Physiol. Revs.*, **23,** 256–278 (1943).
[6] G. O. Burr, *Federation Proc.*, **1,** 224–233 (1942).
[7] G. R. Cowgill, *Physiol. Revs.*, **25,** 664–686 (1945).
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[10] M. M. Piskur, *Oil & Soap,* **22,** 84–100 (1945).
[11] H. E. Longenecker, *Chem. Revs.*, **29,** 201–224 (1941).
[12] H. J. Deuel, Jr., and M. G. Morehouse, *Advances in Carbohydrate Chemistry,* Vol. II, Academic Press, New York, 1946.
[13] T. P. Hilditch, *The Chemical Constitution of the Natural Fats,* Wiley, New York, 1940.
[14] G. S. Jamieson, *Vegetable Fats and Oils,* 2nd ed., Reinhold, New York, 1943.
[15] A. E. Bailey, *Industrial Oil and Fat Products,* Interscience, New York, 1945.
[15a] K. Markley, *Fatty Acids,* Interscience, New York, 1947.

gested food must not be regarded as essential. It is only when the more highly saturated triglycerides are present in such large proportion as to render the fats less digestible that their composition must come under scrutiny insofar as their nutritive value is concerned.

1. Unsaturated Fatty Acid Content

In contrast to the long-chain saturated acids, which animals can synthesize from nonfat sources, certain of the unsaturated fatty acids can be produced by the animal only to a limited degree. Since these are required in such structural capacities as in cell membranes, the need for a continued supply is obviously a vital one. It is therefore evident that, if adequate amounts are to be available for such requirements, they must be supplied in sufficient quantities in the diet.

Oleic acid, $CH_3(CH_2)_7CH{:}CH(CH_2)_7COOH$, is the most common of the unsaturated fatty acids found as a component of both vegetable and animal fats. This acid apparently can be synthesized from saturated acids in adequate quantities; oleins are not considered as essential triglycerides. On the other hand, two other highly unsaturated fatty acids: linoleic acid, $CH_3(CH_2)_4CH{:}CHCH_2CH{:}CH(CH_2)_7COOH$, with two unsaturated linkages; and linolenic acid, $CH_3CH_2CH{:}CHCH_2CH{:}CHCH_2CH{:}CH(CH_2)_7$-COOH, with three double bonds, can satisfy the requirement of the animal for the unsaturated acids. It is also certain that a less widely distributed acid containing four double bonds, arachidonic acid, $C_{20}H_{32}O_2$, also is able to meet the need for the unsaturated fatty acid molecule. According to Arcus and Smedley-Maclean,[16] arachidonic acid has the constitution of $\Delta^{5,\,8,\,11,\,14}$-eicosatetraenoic acid. These workers also confirm the above structure of linoleic acid ($\Delta^{9,\,12}$-octadecadienoic acid).

Linoleic and arachidonic acids are the most effective of these unsaturated acids in satisfying the dietary requirements. Linoleic acid glycerides are widely distributed in vegetable oils, particularly in the seed oils, where linoleic acid may account for as much as 77% of the total fatty acid content (hackberry seed oil). Few quantitative data are available on the linolenic or arachidonic acid content of fats and oils, although in edible oils the quantities must in general be only a fraction of the linoleic acid content. Tables 190 and 191 give values for the essential unsaturated acids reported for common vegetable and animal fats. A casual inspection of the tables will indicate that the seed oils are excellent sources of the essential fatty acids, while in general the animal fats are poor sources of these necessary dietary components. Only in a few cases, after a large intake of the vegetable oils by the animal, can important amounts of the unsaturated acids be found in the animal fats.

[16] C. L. Arcus and I. Smedley-Maclean, *Biochem. J.*, **37,** 1–6 (1943).

TABLE 190

Relative Amounts of Linoleic and Linolenic Acids in Some Common Seed and Other Vegetable Oils

Fat	Essential fatty acid, per cent by weight		Fat	Essential fatty acid, per cent by weight	
	Linoleic	Linolenic		Linoleic	Linolenic
Almond	19.9–17.3[a]	—	Peanut	27.4–13.0[p]	—
Avocado	10.3[b]	—	Perilla seed	33.6[q]	—
Brazil nut	22.8–18.8[c]	—	Pistachio nut	20.0[r]	—
Cocoa butter	21.1[d]	—	Poppy seed	62.2[s]	—
Coconut	2.6–trace[e]	—	Rapeseed	29–10.6[t]	3.5–1[t]
Corn	39.1–34.1[f]	—	Safflower seed	78[u]	—
Cottonseed	50.4–39.4[g]	—	Sesame seed	40.4–36.1[v]	—
Grapeseed	73–43.7[h, i]	0.1[i]	Soybean	58.8–49.3[w]	8.1–2.1[w]
Grapefruit seed	51.4[j]	—	Sunflower seed	68–53.0[u, x]	—
Hackberry tree seed	76.7[k]	—	Tobacco seed	74.5[y]	—
Hempseed	68.8–53.0[l]	24.3–15.9[l]	Tomato seed	38.2[z]	—
Linseed	46.7–3.3[m]	60.9–25.8[m]	Thom apple	74.5[aa]	—
Olive	15.0–3.9[n]	—	Walnut	75.5–50.0[ab]	10.0–2.2[ab]
Palm	10.9–7.5[o]	—	Watermelon seed	65.8[ac]	—

[a] A. Heiduschka and C. Weigemann *J. prakt. Chem.*, **124**, 240–260 (1930); *Chem. Abst.*, **24**, 2907 (1930). B. G. Gunde and T. P. Hilditch, *J. Soc. Chem. Ind.*, **59**, 47–53T (1940).

[b] G. S. Jamieson, W. F. Baughman, and R. M. Hann, *Oil & Fat Ind.*, **5**, 202–207 (1928).

[c] H. A. Schuette and W. W. F. Enz, *J. Am. Chem. Soc.*, **53**, 2756–2758 (1931). H. A. Schuette, R. W. Thomas, and M. Duthey, *ibid.*, **52**, 4114–4117 (1930).

[d] T. P. Hilditch and W. J. Stainsby, *J. Soc. Chem. Ind.*, **55**, 95–101T (1936).

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[k] H. A. Schuette and R. G. Zehrpfenning, *Oil & Soap*, **14**, 269–270 (1937).

[l] H. N. Griffiths and T. P. Hilditch, *J. Soc. Chem. Ind.*, **53**, 75–81T (1934). P. Shestakov and P. Kupchinskii, *Z. deut. Öl- u. Fett-Ind.*, **42**, 741–746 (1922). H. P. Kaufmann and S. Juschkewitsch, *Z. angew. Chem.*, **43**, 90–91 (1930).

[m] H. P. Kaufmann and M. Keller, *Z. angew. Chem.*, **42**, 73–76 (1929). T. P. Hilditch and E. C. Jones, *J. Soc. Chem. Ind.*, **53**, 13–21T (1934). P. J. Gay, *ibid.*, **51**, 126–129T

TABLE 190 (*footnotes continued*)

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[n]T. P. Hilditch and L. Maddison, *J. Soc. Chem. Ind.*, **60,** 258–262T (1941). G. S. Jamieson, R. M. Hann, and W. F. Baughman, *Oil & Fat Ind.*, **4,** 63–65 (1927). T. P. Hilditch, and H. M. Thompson, *J. Soc. Chem. Ind.*, **56,** 434–438T (1934). T. P. Hilditch and E. C. Jones, *J. Chem. Soc.*, **141,** 805–820 (1932). G. S. Jamieson, *Oil & Fat Ind.*, **4,** 426–427 (1927).

[o]T. P. Hilditch and E. C. Jones, *J. Soc. Chem. Ind.*, **49,** 363–368T (1930). A. Banks, H. K. Dean, and T. P. Hilditch, *ibid.*, **54,** 77–82T (1935). T. P. Hilditch and H. Jasperson, *ibid.*, **57,** 84–87T (1938).

[p]A. O. Cruz and A. P. West, *Philippine J. Sci.*, **46,** 199–206 (1931). T. P. Hilditch, M. B. Ichaporia, and H. Jasperson, *J. Soc. Chem. Ind.*, **57,** 363–368T (1938). G. S. Jamieson, W. F. Baughman, and D. H. Brauns, *J. Am. Chem. Soc.*, **43,** 1372–1381 (1921). T. P. Hilditch and E. C. Jones, *J. Soc. Chem. Ind.*, **53,** 13–21T (1934). E. F. Armstrong and J. Allan, *ibid.*, **43,** 201–218T (1924). T. P. Hilditch and N. L. Vidyarthi, *ibid.*, **46,** 172–174T (1927).

[q]H. P. Kaufmann, *Allgem. Oel- u. Fett-Ztg.*, **27,** 39–40 (1930).

[r]D. R. Dhingra and T. P. Hilditch, *J. Soc. Chem. Ind.*, **50,** 9–12T (1931).

[s]A. Eibner and R. Wibelitz, *Chem. Umschau Fette Öle Wachse Harze*, **31,** 109–120, 121–127 (1924).

[t]T. P. Hilditch and H. Paul, *J. Soc. Chem. Ind.*, **54,** 331–336T (1935). R. Yamasaki and K. Ichihari, *Bull. Chem. Soc. Japan*, **11,** 114–117 (1936). T. P. Hilditch, T. Riley, and N. L. Vidyarthi, *J. Soc. Chem. Ind.*, **46,** 457–467T (1927). J. J. Sudborough, H. E. Watson, P. R. Ayyar, and N. R. Damle, *J. Indian Inst. Sci.*, **A9,** 26–42 (1926). K. Täufel and C. Bauschinger, *Z. Untersuch. Lebensm.*, **56,** 253–264 (1928).

[u] R. T. Milner, J. E. Hubbard and M. B. Wills, *Oil & Soap*, **22,** 304–306 (1945).

[v] T. P. Hilditch, M. B. Ichaporia, and H. Jasperson, *J. Soc. Chem. Ind.*, **57,** 363–368T (1938). G. S. Jamieson and W. F. Baughman, *J. Am. Chem. Soc.*, **46,** 775–778 (1924).

[w] W. Kimura, *J. Soc. Chem. Ind. Japan*, **33,** 325B (1930). A. Heiduschka and H. Eger, *Chem. Umschau Fette Öle Wachse Harze*, **38,** 129–130 (1931). F. G. Dollear, P. Krauczunas, and K. S. Markley, *Oil & Soap*, **17,** 120–121 (1940). T. P. Hilditch and E. C. Jones, *J. Soc. Chem. Ind.*, **53,** 13–21T (1934). H. P. Kaufmann, *Allgem. Öel- u. Fett-Ztg.*, **27,** 325–327 (1930). A. O. Cruz and A. P. West, *Philippine J. Sci.*, **48,** 77–88 (1932). W. F. Baughman and G. S. Jamieson, *J. Am. Chem. Soc.*, **44,** 2947–2952 (1922). T. P. Hilditch and H. Jasperson, *J. Soc. Chem. Ind.*, **57,** 84–87T (1938). E. S. Wallis and G. H. Burrows, *J. Am. Chem. Soc.*, **46,** 1949–1953 (1924). T. P. Hilditch and H. Jasperson, *J. Soc. Chem. Ind.*, **58,** 187–189T (1939).

[x] T. P. Hilditch and Y. A. H. Zaky, *Biochem. J.*, **36,** 815–821 (1942). Y. V. Branke and E. F. Gutt, *Bull. Far East. Branch Acad. Sci. U.S.S.R.*, **13,** 17–29 (1935). G. Rankov, *Fette u. Seifen*, **44,** 465–471 (1937). W. F. Baughman and G. S. Jamieson, *J. Am. Chem. Soc.*, **44,** 2952–2957 (1922). A. Eibner, *Farbe u. Lack*, **31,** 463–464, 472–473 (1926). J. Pieraerts, *Mat. grasses*, **17,** 7280–7284, 7340–7343 (1925).

[y] W. L. Roberts and H. A. Schuette, *J. Am. Chem. Soc.*, **56,** 207–209 (1934).

[z] M. P. Gupta and S. Dutt, *J. Indian Chem. Soc.*, **13,** 613–618 (1936).

[aa] T. P. Hilditch and M. B. Ichaporia, *J. Soc. Chem. Ind.*, **55,** 189–190T (1936).

[ab] Y. V. Branke and A. A. Komissarchuk, *Bull. Far East. Branch Acad. Sci. U.S.S.R.*, **14,** 85–102 (1935). G. S. Jamieson and R. S. McKinney, *Oil & Fat Ind.*, **6,** 21–23 (1929). S. Ueno and Y. Nishikawa, *J. Soc. Chem. Ind. Japan*, **40,** 313–314B (1937). H. N. Griffiths and T. P. Hilditch, *J. Soc. Chem. Ind.*, **53,** 75–81T (1934). S. L. Ivanov and E. E. Berdichevski, *Schriften zentral. biochem. Forsch. Inst. Nahr. u. Genussmittelindrie. U.S.S.R.*, **3,** 246–250 (1933). G. S. Jamieson and R. S. McKinney, *Oil & Soap*, **13,** 202 (1936).

[ac] A. J. Nolte and H. W. von Loesecke, *J. Am. Chem. Soc.*, **61,** 889–891 (1939).

TABLE 191

Relative Amounts of Linoleic, Linolenic, and Arachidonic Acids in Some Common Animal Fats

Fat	Essential fatty acid, per cent by weight		
	Linoleic	Linolenic	Arachidonic
Egg yolk (hen)			
Hempseed oil diet	41.9–41.7[a]	10.0–5.2[a]	—
Linseed oil diet	24.9[a]	17.4[a]	—
Various diets	21.7–8.6[a,b,c]	2.9–0.7[a,b,c]	2.3[b] (probably clupanodonic)
Phosphatides	8.2[b]	—	—
Goose fat (body)	19.3[d]	—	—
Hen fat (body)	21.3–17.9[e,f]	—	0.6[e]
Ox depot fat	5.3–1.1[f,g,h]	—	0.5–0.1[h]
Pig depot fat	15.6–0.8[i,j]	—	2.1–0.9[i]
Soybean diet	38.9–31.9[k]	0.5–0.2[k]	—
Peanut diet	19.7[k]	—	—
Cottonseed oil diet (12%)	26.8[l]	—	—
Cottonseed oil diet (8%)	18.2[l]	—	—
Cottonseed oil diet (4%)	13.3[l]	—	—
Sheep depot fat	5–3[m]	—	—
Milk fat (cow)	5.8–2.5[n,o]	—	0.4–0.3[o]
Milk fat (goat)	1.5[p]	—	—
Milk fat (human)	7.9–7.5[q]	5.4–0.3[q]	—
Human fat	11.0–8.3[r]	—	1.0–0.3[r]

[a] E. M. Cruickshank, *Biochem. J.*, **28**, 965–977 (1934).

[b] R. M. Riemenschneider, N. R. Ellis, and H. W. Titus, *J. Biol. Chem.*, **126**, 255–263 (1938).

[c] J. Grossfeld, *Z. Untersuch. Lebensm.*, **65**, 305–311 (1933).

[d] J. Grossfeld, *Z. Untersuch. Lebensm.*, **60**, 64–93 (1930); **62**, 553–566 (1931).

[e] T. P. Hilditch, E. C. Jones, and A. J. Rhead, *Biochem. J.*, **28**, 788–795 (1934).

[f] A. Banks and T. P. Hilditch, *Biochem. J.*, **25**, 1168–1182 (1931).

[g] A. O. Cruz and A. P. West, *Philippine J. Sci.*, **46**, 199–206 (1931).

[h] T. P. Hilditch and H. E. Longenecker, *Biochem. J.*, **31**, 1805–1819 (1937).

[i] A. Banks and T. P. Hilditch, *Biochem. J.*, **26**, 298–308 (1932). H. K. Dean and T. P. Hilditch, *ibid.*, **27**, 1950–1956 (1933).

[j] R. Bhattacharya and T. P. Hilditch, *Biochem. J.*, **25**, 1954–1964 (1931). N. R. Ellis and H. S. Isbell, *J. Biol. Chem.*, **69**, 239–248 (1926). N. R. Ellis and J. H. Zeller, *ibid.*, **89**, 185–197 (1930).

[k] N. R. Ellis and H. S. Isbell, *J. Biol. Chem.*, **69**, 239–248 (1926).

[l] N. R. Ellis, C. S. Rothwell, and W. O. Pool, *J. Biol. Chem.*, **92**, 385–398 (1931).

[m] E. F. Armstrong and J. Allan, *J. Soc. Chem. Ind.*, **46**, 172–174T (1927).

[n] H. K. Dean and T. P. Hilditch, *Biochem. J.*, **27**, 889–897 (1933). T. P. Hilditch and H. M. Thompson, *ibid.*, **30**, 677–691 (1936). T. P. Hilditch and E. E. Jones, *Analyst*, **54**, 75–96 (1929). T. P. Hilditch and J. J. Sleightholme, *Biochem. J.*, **24**, 1098–1113 (1930).

[o] T. P. Hilditch and H. Paul, *Biochem. J.*, **30**, 1905–1914 (1936). T. P. Hilditch and H. E. Longenecker, *J. Biol. Chem.*, **122**, 497–506 (1937–1938). A. R. Baldwin and H. E. Longenecker, *ibid.*, **155**, 407–412 (1945).

[p] D. R. Dhingra, *Biochem. J.*, **28**, 73–78 (1934).

[q] T. P. Hilditch and M. L. Meara, *Biochem. J.*, **38**, 29–34 (1945). A. R. Baldwin and H. E. Longenecker, *J. Biol. Chem.*, **154**, 255–265 (1945).

[r] D. L. Cramer and J. B. Brown, *J. Biol. Chem.*, **151**, 427–438 (1943).

2. Effect of Hydrogenation on Unsaturated Fatty Acid Content

It is logical to suppose that the most unsaturated fatty acids would be first attacked when a fat is hydrogenated. In so-called "selective" hydrogenation, the linoleic acid is largely changed to oleic or iso-oleic acids before the conversion of oleic to stearic acid takes place. The course of the reaction is influenced by the temperature, pressure of hydrogen, the agitation, and the concentration of catalyst.[15] According to Hilditch and Moore,[17] the saturated acids start to increase only after the linoleic acid content is reduced to about 10%. One of their typical results on cottonseed oil is given in Table 192.

TABLE 192

Composition of Cottonseed Oil at Various Stages of Hydrogenation[a]

Sample	Melting point, °C.	Iodine number	Composition of mixed fatty acids, per cent by weight		
			Saturated	Oleic	Linoleic
Original	Liquid	109.1	24.7	23.8	51.5
1	Liquid	100.8	25.0	34.5	34.5
2	26	96.1	25.0	40.5	34.5
3	35	77.4	25.7	60.0	15.0
4	39	72.1	27.2	62.0	11.0
5	40	65.2	27.9	68.5	3.5
6	49	57.5	33.3	67.0	0

[a] T. P. Hilditch and C. W. Moore, *J. Soc. Chem. Ind.*, **42**, 15–17T (1923).

Most of the shortenings made from cottonseed oil melting from 35° to 43° C. and which have an iodine number between 60 and 75, according to Jamieson,[14] have a saturated acid content of 27 to 33%, and an iso-oleic acid content of 7 to 18%. The oleic acid ranges from 37 to 61%, and linoleic acid from 5 to 12%.[18] The iso-oleic acid consists not only of elaidic acid (the *cis*-isomer of oleic acid), but also probably of a $\Delta^{11, 12}$-acid which is also a solid at ordinary temperatures. According to Richardson, Knuth, and Milligan,[19] the iso-oleic acid concentration may reach a maximum of 24.8% in the hydrogenation of cottonseed oil.

B. Fats as Sources of Vitamins

Because of their unique solvent action, fats are excellent carriers of the so-called fat-soluble vitamins. Moreover, the most efficient absorption of these vitamins from the gastro-intestinal tract would seem to require

[17] T. P. Hilditch and C. W. Moore, *J. Soc. Chem. Ind.*, **42**, 15–17T (1923).

[18] According to a personal communication from G. O. Burr, hydrogenation reduces the linoleic acid to a value probably below 5%. The biological activity does not agree with the value calculated from the iodine and thiocyanogen numbers.

[19] A. S. Richardson, C. A. Knuth, and C. H. Milligan, *Ind. Eng. Chem.*, **16**, 519–522 (1924).

the simultaneous absorption of neutral fat. Although certain fish liver oils must be considered as the most concentrated sources of vitamins A and D, the vegetable sources may offer a considerable proportion of our daily intake. As far as vitamin E is concerned, the vegetable oils are the chief source.

1. Vitamin A and Provitamin A

The main proportion of potential vitamin A in a well balanced diet comes from the provitamin A present in such vegetables as turnip greens, spinach, and broccoli, as well as in such yellow-colored foods as squash, carrots, apricots, and persimmons. β-Carotene is the most effective provitamin A, while α-carotene and cryptoxanthine are about 50% as effective,[20, 21] and γ-carotene is only one-fourth as good [22] as the β-carotene.

In most cases, provitamin A in vegetables is present with a minimum amount of fat. The oils present in the storage depots in the seeds are as a rule largely free of provitamin A. On the other hand, the oils from the outer coverings or cortex of the seeds sometimes contain appreciable amounts of carotene.[23] The notable exception among the vegetable oils, as far as carotene content is concerned, is red palm oil. Buckley [24] has reported levels as high as 1,900 I.U.[25] of vitamin A per g. in the oil from the ripe fruit. In the over-ripe fruit, the content was reduced to 1,600 I.U. per g., while in oil from the green fruit only 600 I.U per g. were present. The vitamin A value found for the oil from the ripe fruit equals that in a good grade of cod-liver oil and is 60 times the average of good butter. Kaufmann [26] has confirmed these values since he reports carotene levels in red palm oils varying between 0.20 and 0.05%. If the carotenoid is largely β-carotene, the maximum level would correspond to a vitamin A potency in excess of 3,000 I.U. per g. Rosedale [27] has also reported a high potency for the red palm oil of Malaya (*Elaeis guineensis*), and its use in India, to augment the vitamin A intake, has been recommended.[28] It could be used with hydrogenated fat or coconut oil as a margarine or for a cooking fat.[29] Palm oil has proved as valuable as cod-liver oil in the treatment of keratomalacia in Madras.

[20] H. J. Deuel, Jr., E. Sumner, C. Johnston, A. Polgár, and L. Zechmeister, *Arch. Biochem.*, **6,** 157–161 (1945).

[21] H. J. Deuel, Jr., E. R. Meserve, C. Johnston, A. Polgár, and L. Zechmeister, *Arch. Biochem.*, **7,** 447–450 (1945).

[22] H. J. Deuel, Jr., C. Johnston, E. Sumner, A. Polgár, W. A. Schroeder, and L. Zechmeister, *Arch. Biochem.*, **5,** 365–371 (1944).

[23] W. J. Blackie and G. R. Cowgill, *Food Research*, **4,** 129–133 (1939).

[24] T. A. Buckley, *Malayan Agr. J.*, **24,** 485–488 (1926).

[25] I.U. refers to International Units; 1 I.U. of vitamin A is equivalent to the effect of 0.6 μg. of pure β-carotene.

[26] H. P. Kaufmann, *Fette u. Seifen*, **48,** 53–59 (1941).

[27] J. L. Rosedale, *Chemical Analyses of Malayan Foods*, Singapore Government Printer, Singapore, 1935.

[28] Indian Research Fund Association, *J. Indian Med. Assoc.*, **6,** 539 (1937), cited from footnote 7.

[29] N. K. De, *Indian J. Med. Research*, **25,** 11–15 (1937).

Vitamin A, as such, is never found in vegetable oils unless they have been fortified with it. In butter, the potential vitamin A is present both in the form of vitamin A and β-carotene. It was believed earlier that the average vitamin A content of butter approximated 9,000 I.U. per pound; the standard for fortification of margarine set by the Food and Drug Administration in 1941 was based on this figure.[30] However, a recent survey [31] made throughout all seasons of the year in a number of sections of the United States has indicated an average of 15,000 I.U. of vitamin A per pound of butter. The margarine manufacturers have now, in most instances, increased the vitamin A level of their products to this value.

2. Vitamin D and Provitamin D

No appreciable quantity of vitamin D has been found in any vegetable oil except coconut oil. A certain quantity is probably synthesized in this case by the action of the sunlight on the provitamin D while the coconut is being dried in the preparation of copra, but the amounts so produced must be quite variable. The sterols which are present in vegetable oils and which are capable of being activated to a vitamin D by various means (chiefly ultraviolet light) are listed in Table 193. Ergosterol is the most

TABLE 193

Phytosterols Present in Different Vegetable Fats

Phytosterol	Formula	Plant source
Active as Provitamin D		
Ergosterol	$C_{28}H_{46}O$	Ergot oil, yeast
Dihydroergosterol	$C_{28}H_{46}O$	Ergot oil, yeast
Dihydrositosterol	$C_{29}H_{52}O$	Various fats except cottonseed and linseed oils
Inactive as Provitamin D		
Brassicasterol	$C_{28}H_{46}O$	Rapeseed oil
Sitosterol	$C_{29}H_{50}O$	Corn oil
Stigmasterol	$C_{29}H_{48}O$	Calabar bean fat, coconut, corn, rapeseed, and other oils
Zymosterol	$C_{27}H_{44}O$	Yeast fat

effective provitamin D, while dihydroergosterol and dihydrositosterol follow in that order. Sitosterol and stigmasterol are only active as their 7-dehydro compounds. Although the phytosterols are usually present in concentrations considerably under 1%, stigmasterol exceeds that figure in the calabar bean fat.[32]

[30] W. B. Miller, *Federal Register,* **6,** 2761–2763 (1941).
[31] *U.S. Dept. Agr. Misc. Pub.,* **No. 571** (1945).
[32] A. Windaus and A. Hauth, *Ber.,* **39,** 4378–4384 (1906).

3. α-Tocopherol (Vitamin E)

The requirement for vitamin E can best be supplied by α-tocopherol 5,7,8-trimethyltocol), but β-tocopherol (5,8-dimethyltocol) and γ-tocopherol (7,8-dimethyltocol) also are possibly effective but to a somewhat lesser degree. A potent preparation of the mixed esters prepared by molecular distillation of vegetable oils is available commercially, as is synthetic

TABLE 194

Tocopherol (Vitamin E) Content of Some Vegetable and Animal Fats and Oils

Oil or fat	Tocopherol content, mg. per 100 g.	Oil or fat	Tocopherol content, mg. per 100 g.
Vegetable		Vegetable	
Babassu, crude	3[a]	Safflower, crude	80[a]
Castor	50[a]	Sesame, refined	50[a]
Coconut, refined	3[a]	Soybean, crude	212, 152[b]
Coconut, hydrogenated	3[b]	Soybean, refined	175, 125[b]; 110[a]
Corn, crude	119[b]	Soybean, phosphatide	200[c]
Corn, refined	95[a]	Wheat germ, crude	400[a]; 380, 310[b]
Cottonseed, crude	100[b]	Wheat germ, solvent extracted	550[a]
Cottonseed, refined	90[a]	Animal	
Olive	20[a]; 25[b]	Cod liver	26[b]
Palm, crude	50[a]	Lard, prime steam	2.8–2.1, 0.8–0.5[d]; 0.5[a]; 0.2[e]
Peanut, crude	52[a]		
Peanut, refined	48[a]		
Pecan, refined	45[a]	Mangona shark liver	10[f]
Rice bran, crude	100[a]	Oleo oil	2[a]
Rice bran, refined	90[a]	Soupfin shark liver	4[f]

[a] A. E. Bailey, *Industrial Oil and Fat Products*, Interscience, New York, 1945.
[b] F. W. Quackenbush, H. L. Gottlieb, and H. Steenbock, *Ind. Eng. Chem.*, **33**, 1276–1278 (1941).
[c] J. L. Jensen, K. C. D. Hickman, and P. L. Harris, *Proc. Soc. Exptl. Biol. Med.*, **54**, 294–295 (1943).
[d] J. R. Chipault, W. O. Lundberg, and G. O. Burr, *Arch. Biochem.*, **8**, 321–335 1945).
[e] P. Karrer and H. Keller, *Helv. Chim. Acta*, **21**, 1161–1169 (1938); **22**, 253–259 (1939); **22**, 617–618 (1939); **23**, 464–465 (1940).
[f] C. D. Robeson and J. G. Baxter, *J. Am. Chem. Soc.*, **65**, 940–943 (1943).

α-tocopherol. While it is uncertain whether or not vitamin E plays a role as an antisterility vitamin in the human, it is important in the treatment of some types of muscular dystrophy. Moreover, it is of importance as an antioxidant for fats and it is necessary in the diet if vitamin A is to be effectively utilized. Miller [33] found that the vitamin E present in vegetable oils is not destroyed by the usual processes of hydrogenation. In fact, Weber, Irwin, and Steenbock [34] have employed a commercial hydrogenated shortening, made by the hydrogenation of cottonseed oil to an iodine number of 70, as an excellent and stable source of vitamin E. Evans and

[33] H. G. Miller, *J. Nutrition*, **26**, 43–50 (1943).
[34] J. Weber, M. H. Irwin, and H. Steenbock, *Am. J. Physiol.*, **125**, 593–600 (1939).

Burr,[35, 36] and later Cummings and Mattill [37] also demonstrated that hydrogenated cottonseed oil is a more reliable source of vitamin E than the unhydrogenated oil.

Vitamin E is chiefly found in vegetable fats but it has been proved to be present in appreciable concentration in several fish liver oils. The most concentrated natural source is wheat germ oil. The tocopherol content of some vegetable and animal oils is given in Table 194.

4. Vitamin K

This vitamin is present to a considerable extent in hempseed and soybean oil. It is a necessary adjunct in stimulating, in the liver, the production of prothrombin, a protein essential for the clotting of blood. Since the water-soluble derivatives of 2-methyl-1;4-naphthoquinone are considerably more effective than the natural forms of vitamin K, and intestinal synthesis usually provides an adequate source, little attention has been paid to food sources of this vitamin.

5. Choline

Choline is now considered one of the members of the vitamin B complex. Although choline itself is water-soluble, it is chiefly found in nature in a combined form as a component of lecithin. Crude lecithin is prepared commercially from soybean oil in 30–35% concentration. It is widely used as a wetting or emulsifying agent in margarines, candies, bakery products, and pharmaceutical preparations.[38, 39] Choline is important in nutrition since it prevents the accumulation of fat in the liver. Hence it is referred to as a lipotropic agent.

Slanetz and Scharf [40, 41] have recently shown that commercial soybean lecithin contains a principle which markedly increases the level of storage of vitamin A in the liver of rats. The effect noted was not given by choline. Patrick and Morgan [42] had previously obtained a similar result on the chick. It is believed that the substance may be also extracted from yeast by fat solvents.[41] Jensen, Hickman, and Harris [43] have suggested that the effect obtained by Slanetz and Scharf is caused by vitamin E. However, Patrick and Morgan,[44] and Scharf and Slanetz [45] more recently

[35] H. M. Evans and G. O. Burr, "The Antisterility Vitamin, Fat-Soluble E," Univ. Calif. *Memoirs,* **8** (1927).
[36] H. M. Evans and G. O. Burr, *J. Am. Med. Assoc.,* **89,** 1587–1590 (1927).
[37] M. J. Cummings and H. A. Mattill, *J. Nutrition,* **3,** 421–432 (1931).
[38] J. Eichberg, *Oil & Soap,* **16,** 51–54 (1939).
[39] G. A. Wiesehahn, *Oil & Soap,* **14,** 119–122 (1937).
[40] C. A. Slanetz and A. Scharf, *J. Nutrition,* **30,** 239–243 (1945).
[41] C. A. Slanetz and A. Scharf, *Proc. Soc. Exptl. Biol. Med.,* **53,** 17–19 (1943).
[42] H. Patrick and C. L. Morgan, *Science,* **98,** 434–435 (1943).
[43] J. L. Jensen, K. C. D. Hickman, and P. L. Harris, *Proc. Soc. Exptl. Biol. Med.,* **54,** 294–295 (1943).
[44] H. Patrick and C. L. Morgan, *Poultry Sci.,* **23,** 525–528 (1944).
[45] A. Scharf and C. A. Slanetz, *Proc. Soc. Exptl. Biol. Med.,* **57,** 159–161 (1944).

have suggested that the vitamin A effect of the lecithin preparation is caused by some substance other than vitamin E. Just how widely distributed such a factor may be in fats and oils will await further work on its identification.

A possible explanation of the effects reported for soybean lecithin is that it contains highly unsaturated acids of the C_{20}–C_{22} series. Hilditch and Zaky [46] have reported that six seed phosphatides examined by them (cottonseed, sunflower seed, rapeseed, soybean, peanut, and linseed) contained 3–6% of the unsaturated C_{20}–C_{22} acids which were not present in the glyceride fraction. In the majority of cases, linoleic acid forms 40–55% of the total acids of the seed phosphatides. Hilditch and Zaky suggest that, in addition to linoleic acid, arachidonic and possibly mixtures of polyethenoid C_{20} and C_{22} acids are also present. The high nutritive value of arachidonic acid has been demonstrated.[47–50] It has also been reported that lecithin tends to increase the absorption of fat,[50a] as well as of vitamin A.[51]

6. Inositol

Inositol or inosite is another member of the B complex which has recently been shown to occur as a lipid conjugate. Chemically, it is hexahydrocyclohexane ($C_6H_{12}O_6$). It was discovered in the free state as a component of muscle tissue; its hexaphosphate, phytin, is also a well-known constituent of wheat bran. Dragstedt *et al.*[52] separated a lipotropic agent from pancreas which they called "lipocaic"—the active principle of which is now believed to be identical with inositol.

Klenk and Sakai [53] found that inositol monophosphate was a component of crude soybean lecithin. Its presence has been demonstrated in the phosphatides of brain and spinal cord,[54] from which it is extractable only after hydrolysis. Woolley [55] purified this phosphatide and found it had a uniform inositol content of 16%, which was not altered by recrystallization. In addition to inositol, the purified phosphatide gave phosphoric and oleic acids, saturated fatty acids, traces of ethanolamine, and tartaric acid upon hydrolysis. This so-called "lipositol" was found to make up

[46] T. P. Hilditch and Y. A. H. Zaky, *Biochem. J.*, **36,** 815–821 (1942).
[47] E. M. Hume, L. C. A. Nunn, I. Smedley-Maclean, and H. H. Smith, *Biochem. J.*, **34,** 879–883 (1940).
[48] I. Smedley-Maclean and L. C. A. Nunn, *Biochem. J.*, **34,** 884–902 (1940).
[49] O. Turpeinen, *J. Nutrition,* **15,** 351–366 (1938).
[50] G. O. Burr, J. B. Brown, J. P. Kass, and W. O. Lundberg, *Proc. Soc. Exptl. Biol. Med.*, **44,** 242–244 (1940).
[50a] V. Augur, H. S. Rollman, and H. J. Deuel, Jr., *J. Nutrition*, **33,** 177–186 (1947).
[51] D. Aldersberg and H. Sobotka, *J. Nutrition,* **25,** 255–263 (1943).
[52] L. R. Dragstedt, J. V. Prohaska, and H. P. Harms, *Am. J. Physiol.*, **117,** 175–181 (1936).
[53] E. Klenk and R. Sakai, *Z. physiol. Chem.*, **258,** 33–38 (1939).
[54] J. Folch and D. W. Woolley, *J. Biol. Chem.*, **142,** 963–964 (1942).
[55] D. W. Woolley, *J. Biol. Chem.*, **147,** 581–591 (1943).

about 18% of the total phosphatides in the soybean. An inositol-containing phosphatide has also been prepared from bovine tubercle bacillus,[56] as well as from the human tubercle bacillus.[57]

C. Effect of Rancidity on Composition of Fat

Although it has long been recognized that nutrition may be seriously hampered in animal tests when diets become rancid, it was believed that this was largely to be ascribed to the failure of the animals to eat, due to the distastefulness of the diet. Recently, it has been shown that there is an actual destruction of several of the essential principles in the diet under such conditions.

Since rancidity develops by the formation of peroxides of the unsaturated fatty acids, it is apparent that the fat-soluble vitamins would be the constituents most readily acted upon by the pro-oxidants. Although the most susceptible vitamins are carotene and vitamin E, there is some evidence also that vitamin D may be somewhat sensitive.[58]

1. Carotene and Vitamin A

A number of investigators have found that the effectiveness of carotene supplements, when fed in conjunction with a diet free of vitamin A, vary with the solvent in which the provitamin is dissolved. Lathbury and Greenwood [59] obtained considerably better results when peanut oil, rather than coconut oil, was used as the solvent. Kraybill and Shrewsbury [60] reported that three times as much carotene was required to produce an equal growth when decolorized butterfat was the solvent as when cottonseed oil was used, while Basu [61] found that carotene or vitamin A, when tested with several oils, gave the best growth when fed in linseed oil and the poorest in peanut oil. De [62] also showed that carotene in aramanth was less satisfactory than carotene fed as a constituent of red palm oil. Sherman [63] found that soybean oil gave the best growth when fed to rats on a controlled intake of carotene. Cottonseed, linseed, corn, and wheat germ oils also gave a beneficial effect, but butterfat and coconut oil had no appreciable value. The different responses could not be correlated with a variation in carotene absorption or with the methyl linoleate content when this compound formed the fatty constituent of the diet. In fact, methyl

[56] J. Cason and R. J. Anderson, *J. Biol. Chem.*, **126,** 527–541 (1938).
[57] R. J. Anderson, W. C. Lothrop, and M. M. Creighton, *J. Biol. Chem.*, **125,** 299–308 (1938).
[58] J. C. Fritz, J. L. Halpin, J. H. Hooper, and E. H. Kramke, *Ind. Eng. Chem.*, **34,** 979–982 (1942).
[59] K. C. Lathbury and G. N. Greenwood, *Biochem. J.*, **28,** 1665–1673 (1934).
[60] H R. Kraybill and C. L. Shrewsbury, *J. Nutrition,* **11,** 103–110 (1930).
[61] N. K. Basu, *Z. Vitaminforsch.*, **6,** 106–110 (1937).
[62] N. K. De, *Indian J. Med. Research,* **24,** 751–766 (1937).
[63] W. C. Sherman, *J. Nutrition,* **22,** 153–165 (1941).

linoleate had a depressing effect on carotene utilization, unless an excess of carotene was given. Under the latter conditions, a stimulatory effect on growth was noted. It was also shown by Quackenbush *et al.*[64] that the depressing effect of the pure linoleate could be overcome by an excess of tocopherol.

It is now recognized that these variations in effect with the different oils are associated with their tocopherol content. Maximum growth can only be attained on given levels of carotene or vitamin A when optimum amounts of the α-tocopherol are present.[65, 66] It is not clear whether this effect of tocopherol is to be ascribed to its protective action against the pro-oxidant—thus preventing the destruction of vitamin A or carotene—or to a synergistic relationship between tocopherol and vitamin A.

2. α-Tocopherol

Although tocopherol itself is an excellent antioxidant, it possesses this characteristic because of its ready oxidizability. It is particularly susceptible to destruction by rancid fats. On diets low in vitamin E, sterility occurs when rancidity develops because vitamin E is destroyed.[67] Because of the slower development of rancidity in hydrogenated fats than in lard, fertility has been shown to be retained when the lard is replaced by hydrogenated fats with a resulting sparing of the vitamin E.[34, 36]

3. Water-Soluble Vitamins

Water-soluble vitamins are also susceptible to destruction when they are subjected to the action of rancid fat. Biotin has been shown to be destroyed.[68] There is also evidence that ascorbic acid, which is also a fat antiovidant, may be destroyed by rancidity,[69] although Burr and Barnes [5] report a negative effect with pure ascorbic acid.

4. Unsaturated Fatty Acids

In the peroxidation of the natural fats, linoleic acid naturally tends to be destroyed. As a result, skin conditions, which resemble those obtained in fat deficiency but which are more severe, have been shown to occur in rats [70] and in dogs [71] which have received a rancid diet over a period of time.

[64] F. W. Quackenbush, R. P. Cox, and H. Steenbock, *J. Biol. Chem.*, **145,** 169–177 (1942).
[65] K. Hickman, P. L. Harris, and M. R. Woodside, *Nature*, **150,** 91–92 (1942).
[66] P. L. Harris, M. W. Kaley, and K. C. D. Hickman, *J. Biol. Chem.*, **152,** 313–320 (1944).
[67] H. A. Mattill, *J. Am. Med. Assoc.*, **89,** 1505–1508 (1927).
[68] P. L. Pavcek and G. M. Shuli, *J. Biol. Chem.*, **146,** 351–355 (1942).
[69] C. Golumbic and H. A. Mattill, *J. Am. Chem. Soc.*, **63,** 1279–1280 (1941).
[70] D. V. Whipple, *Oil & Soap*, **10,** 228–229 (1933).
[71] D. V. Whipple, *Proc. Soc. Exptl. Biol. Med.*, **30,** 319–321 (1932).

5. Additional Symptoms Resulting from Ingestion of Rancid Fats

Anemia has been noted when rats were fed on a synthetic diet containing thiamin, riboflavin, pyridoxine, and pantothenic acid, together with crude linoleic acid.[72] The rats lost weight but this could be counteracted by feeding yeast. Somewhat similar results were recorded by Barnes and Burr,[5] when the destructive agent was rancid lard. Both the red and white blood cell count fell. There was no evidence of vitamin A deficiency, but yeast prevented the anemia, as well as the development of rancidity.

Reproductive failure other than that due to the absence of vitamin E has been reported,[73] although this has been denied by Deathesage *et al.*[74] Although carcinogenic properties have been ascribed to rancid fats, the toxicity of fats in which rancidity was produced by copper oleate or ultraviolet light has been found to be no greater than that of the fresh fat.[75, 76]

Burr and Barnes [5] suggests that rancidity may exert its harmful effects not only by destroying essential components in the diet, but possibly by continuing its deleterious action after deposition in the tissues. Although it was not possible to improve the stability of the body fat of rats by increasing the anti-oxidants in a normal diet, the body fat from vitamin E-deficient rats had a reduced keeping time and this could be increased by α-tocopherol, but not by yeast or hydroquinone.[77] Quackenbush [78] has recently published a review on rancidity in relation to the nutritive value of fats.

III. Various Indices for Evaluation of Nutritive Value of Fats

A. Extent of Digestibility

Foodstuffs are defined as substances which have the capability of being added to the body's substance or, when absorbed into the blood stream, of preventing or reducing the wasting of some necessary constituent of the organism.[79] The first prerequisite for any such utilization must be absorption from the gastro-intestinal tract. It is obvious that the nutritive value of a fat must be in proportion to its digestibility.

The "coefficient of digestibility" is the usual index for expressing the degree of absorption. By this term is meant the percentage of the ingested

[72] P. György, R. Tomarelli, R. P. Ostergard, and J. B. Brown, *J. Exptl. Med.*, **76,** 413–420 (1942).
[73] B. A. Kudrjashov, *Arch. Exptl. Path. Pharmakol.*, **169,** 275–289 (1933).
[74] F. E. Deathesage, K. P. McConnell, and H. A. Mattill, *Proc. Soc. Exptl. Biol. Med.*, **46,** 399–402 (1941).
[75] P. S. Lavik and C. A. Baumann, *Cancer Research,* **1,** 181–187 (1941).
[76] P. S. Lavik and C. A. Baumann, *Cancer Research,* **3,** 749–756 (1943).
[77] R. H. Barnes, W. O. Lundberg, H. T. Hanson, and G. O. Burr, *J. Biol. Chem.*, **149,** 313–322 (1943).
[78] F. W. Quackenbush, *Oil & Soap,* **22,** 336–338 (1945).
[79] G. Lusk, *The Science of Nutrition,* 3rd ed., Saunders, Philadelphia, 1928, p. 186.

foodstuff which is absorbed. It is usually calculated after making allowances for the metabolic fat which is determined in control experiments with fat-free diets.

1. Vegetable and Animal Fats with Melting Points below 50° C.

All natural fats in the above category are practically completely digested in the normal individual. The only exceptions occur in those cases where powerful irritants are present in the oils, as in castor or

TABLE 195

Average Coefficients of Digestibility of Different Vegetable Fats and Oils Fed to Man

Fat or oil	Number of experiments	Average daily fat intake, g.	Coefficient of digestibility
Almond[a]	4	70	97.1
Apricot kernel[b]	4	68	98.4
Avocado[c]	3	100	87.8
Black walnut[a]	4	56	97.5
Brazil nut[a]	3	81	96.3
Butternut[a]	3	43	95.4
Charlock[d]	4	60	98.9
Cherry kernel[c]	4	57	98.0
Cocoa butter[e]	11	51	94.9
Coconut[e,f]	12	65	97.9, 88.7
Cohune[c]	4	52	99.1
Corn[d,f]	7	78	96.9
Cottonseed[e,f]	12	86	97.6, 96.9
Cupuassu[c]	4	41	94.1
English walnut[a]	3	78	97.6
Hempseed[c]	3	57	98.5
Hickory nut[a]	4	95	99.3
Japanese mustard seed[d]	3	79	95.8
Java almond[g]	2	60	97.0
Melon seed[b]	3	40	98.2
Olive[e]	10	73	97.8
Palm kernel[e]	4	100	98.0
Peach kernel[b]	3	60	96.6
Peanut[e]	5	98	98.3
Pecan[a]	4	104	96.8
Poppy seed[c]	7	50	96.3
Pumpkin seed[b]	2	75	98.2
Rapeseed[d]	4	82	98.8
Sesame[e]	5	90	98.0
Soybean[d,f]	7	80	97.5, 93.7
Sunflower seed[d]	4	90	96.5
Tea seed[g]	1	49	91.2
Tomato seed[b]	3	57	95.8
Watermelon seed[g]	3	30	94.8

[a] A. D. Holmes, *U.S. Dept. Agr. Bull.*, **No. 630** (1916).
[b] A. D. Holmes, *U.S. Dept. Agr. Bull.*, **No. 781** (1919).
[c] A. D. Holmes and H. J. Deuel, Jr., *J. Biol. Chem.*, **41**, 227–235 (1920).
[d] A. D. Holmes, *U.S. Dept. Agr. Bull.*, **No. 687** (1918).
[e] C. F. Langworthy and A. D. Holmes, *U.S. Dept. Agr. Bull.*, **No. 505** (1917).
[f] L. R. Holt, Jr., H. C. Tidwell, C. M. Kirk, D. M. Cross, and S. Neale, *J. Pediatrics*, **6**, 427–480 (1935). These second experiments were on normal infants.
[g] H. J. Deuel, Jr., and A. D. Holmes, *U.S. Dept. Agr. Bull.*, **No. 1033** (1922).

croton oil. Absorption in the latter case is prevented by a premature expulsion of the material from the small intestine before lipolysis and absorption have been able to take place.

According to Bernton *et al.*,[80] the water-soluble allergens in the cottonseed embryo are completely absent from refined cottonseed oil. The subject of allergens in cottonseed products is discussed in Chapter VIII.

TABLE 196

Average Coefficients of Digestibility of Different Animal Fats and Oils Fed to Man

Fat or oil	Number of experiments	Average daily fat intake, g.	Coefficient of digestibility
Beef (m.p. 45°C.)[a]	10	100	93
Brisket[b]	7	80	97.4
Butter[a,c]	8	100	97, 88.9
Chicken[b]	8	95	96.7
Cod-liver[d]	4	47	97.7
Cream[b]	7	78	96.9
Egg yolk[b]	6	83	93.8
Fish[b]	3	60	95.2
Goat's butter[e]	4	43	98.4
Goose[b]	7	95	95.2
Hard palate (m.p. 34°C.)[e]	3	88	93.7
Horse[e]	3	63	93.9
Kid[e]	3	60	95.3
Lard[a]	9	90	97
Oleo[e]	8	57	96.8
Ox marrow[e]	4	87	93.5
Ox tail[e]	3	74	96.6
Turtle[e]	4	46	98.6

[a] C. F. Langworthy and A. D. Holmes, *U.S. Dept. Agr. Bull.*, **No. 310** (1915).
[b] C. F. Langworthy and A. D. Holmes, *U.S. Dept. Agr. Bull.*, **No. 507** (1917).
[c] L. R. Holt, Jr., H. C. Tidwell, C. M. Kirk, D. M. Cross, and S. Neale, *J. Pediatrics*, **6**, 427–480 (1935). The second experiment was on a normal infant.
[d] H. J. Deuel, Jr., and A. D. Holmes, *U.S. Dept. Agr. Bull.*, **No. 1033** (1922).
[e] A. D. Holmes, *U.S. Dept. Agr. Bull.*, **No. 613** (1919).

The most complete study of the digestibility of fats in man was made over a period of years in the Office of Home Economics of the United States Department of Agriculture. These data have been summarized by Langworthy.[81] Table 195 presents the results on various vegetable fats and oils, while Table 196 gives a similar analysis of animal fats.

A superficial examination of the data summarized in Tables 195 and 196 shows that the animal and vegetable fats are equally well digested when taken in amounts of 50 to 100 g. daily by men. With the exception of two low results (87.8 for avocado and 91.2 for tea seed oil), the average coefficient of digestibility of the 34 vegetable fats studied varied between

[80] H. S. Bernton, J. R. Spies, and H. Stevens, *J. Allergy*, **11**, 138–146 (1940).
[81] C. F. Langworthy, *Ind. Eng. Chem.*, **15**, 276–278 (1923).

94.2 and 99.3. Of the 19 animal fats investigated, all were in the range between 93.5 and 98.6.

Tidwell, Holt, Farrow, and Neale [82] found that both olive and soybean oils were better absorbed in premature infants than was butterfat. Smith,[83] experimenting on 80 men and women, found objective gastric and intestinal symptoms more than four times as frequently when lard was used in food preparation as when hydrogenated vegetable fat was used. Corn oil and cottonseed oil both have been shown to be 99% digestible in dogs.[84]

2. Vegetable and Animal Fats with Melting Points over 50° C.

In contrast to the practically complete digestibility of animal and vegetable fats where the melting points are under 50° C., numerous investigators have reported that higher melting fats are less completely absorbed. Langworthy and Holmes [85] have stated that "of the fats tested, the fats of low melting point are capable of more complete assimilation than those of high melting point."

Deuel and Holmes [86] have suggested that an inverse relationship exists between the extent of absorbability and the melting point. Digestibility experiments on human subjects with high-melting natural fats and with hydrogenated fats (both blended and where the entire fat was subjected to partial hydrogenation) are recorded in Table 197.

A similar relationship to that found in man, between melting point and digestibility, has been reported by Evans and Lepkovsky [87] for the rat. All the low-melting oils studied had digestibilities of 97 to 98%. On the other hand, the coefficient of digestibility of almost completely hydrogenated cottonseed oil (m.p. 62.5° C.) was approximately 38 while that of highly hydrogenated perilla oil (m.p. 67.5° C.) approached zero (11 and 1, respectively, in two tests). In control tests on partially hydrogenated cottonseed oil (m.p. 42° C.), the digestibility exceeded 91%.

However, Hoagland and Snider [88] did not find a consistent relationship between melting point and digestibility in their tests on rats. When the fats made up 5% of the diet, the following coefficients of digestibility were observed: coconut oil, 98.9; soybean oil, 98.5; corn oil, 97.5; butterfat, 88.3; mutton tallow, 74.6; oleo stock, 74; and cocoa butter, 63.3.

(a) Digestibility of Tristearin. The less complete availability of the higher melting fats may be largely attributable to the increasing pro-

[82] H. C. Tidwell, L. E. Holt, Jr., H. L. Farrow, and S. Neale, *J. Pediatrics,* **6,** 481–489 (1935).
[83] C. S. Smith, *Ohio State Med. J.,* **39,** 425–428 (1943).
[84] E. W. Rockwood and P. B. Sivickes, *J. Am. Med. Assoc.,* **71,** 1649–1650 (1918).
[85] C. F. Langworthy and A. D. Holmes, *U.S. Dept. Agr. Bull.,* **No. 310** (1915).
[86] H. J. Deuel, Jr., and A. D. Holmes, *Am. J. Physiol.,* **54,** 479–488 (1921).
[87] H. M. Evans and S. Lepkovsky, *J. Biol. Chem.,* **96,** 165–177 (1932).
[88] R. Hoagland and G. G. Snider, *J. Nutrition,* **25,** 295–302 (1943).

portion of tristearin. Arnschink,[89] many years ago, found that dogs could utilize only about 10% of the pure tristearin fed. The balance was excreted in the stool as unhydrolyzed triglyceride. Hoagland and Snider[90] have obtained similar results on rats; tristearin was found to be absorbed only

TABLE 197

Average Coefficients of Digestibility in Man of Some High-Melting Fats and Some Hydrogenated Fat Mixtures

Fat or oil	Melting point, °C.	Number of experiments	Average daily fat intake, g.	Coefficient of digestibility
Mutton[a]	50	7	53	88
Oleostearin[b,e]	50	3	66	80.1
Deer[c]	51.4	3	46	81.7
Hydrogenated fats[d]				
Cottonseed	35	5	—	96.8
	46	3	—	94.9
Peanut	37	5	—	98.1
	39	3	—	95.9
	43	5	—	96.5
	50	4	—	92.0
	52.4	3	—	79.0
Corn	33	5	—	94.7
	43	5	—	95.4
	50	5	—	88.5
Blended hydrogenated fats[e]				
Cottonseed				
(12.5 : 87.5)[f]	45.8	2	52.6	96.4
(18.8 : 81.2)	47.8	4	76.3	94.2
(23.5 : 76.5)	48.1	2	49.4	94.4
(22.1 : 77.9)	50.0	3	56.9	87.0
Peanut				
(6.2 : 93.8)	43.0	5	73.8	96.6
(9.1 : 90.9)	43.2	4	79.7	97.4
(33.3 : 66.7)	51.1	4	90.3	92.8
Corn				
(9.1 : 90.9)	39	4	102.9	95.2
(25.0 : 75.0)	49	3	105.4	93.3
(30.8 : 69.2)	54	3	92.5	91.5

[a] C. F. Langworthy and A. D. Holmes, *U.S. Dept. Agr. Bull.*, **No. 310** (1915).
[b] A. D. Holmes, *U.S. Dept. Agr. Bull.*, **No. 613** (1919).
[c] H. J. Deuel, Jr., and A. D. Holmes, *U.S. Dept. Agr. Bull.*, **No. 1033** (1922).
[d] H. J. Deuel, Jr., and A. D. Holmes, *Am. J. Physiol.*, **54,** 479–488 (1921). In these tests, all of the oil was subjected to partial hydrogenation to give fats of the varying melting points.
[e] A portion of the fats was almost completely saturated with hydrogen and blended with sufficient untreated oil to give mixtures of the melting points indicated.
[f] The values in parentheses indicate the respective proportions of completely saturated fat and untreated oil mixed in the fat blend.

to the extent of 6 and 8%, respectively, in two series of tests. Tripalmitin, however, was largely utilized in the rat (84 and 82%); these figures correspond closely to others obtained in earlier experiments on dogs.[91]

[89] L. Arnschink, *Z. Biol.*, **26,** 434–451 (1890).
[90] R. Hoagland and G. G. Snider, *J. Nutrition*, **26,** 219–226 (1943).
[91] J. F. Lyman, *J. Biol. Chem.*, **32,** 7–11 (1917).

(b) Fatty Acids vs. Triglycerides. It was suggested by Lyman[91] that the melting point is not the sole consideration in determining the extent of absorption. He found that, while dogs were able to utilize 95% of administered tripalmitin, they could absorb only 82% when fed palmitic acid. A similar difference has recently been reported for the rat,[90] in which case the digestibility of palmitic acid at the 10% level was only 37% as compared with 82% for its triglyceride.

(c) Concentration of Fat in Diet. Some of the inconsistencies in the results of different investigators may be related partly to variations in intake. Whereas the digestibility of stearic acid somewhat increased with a higher concentration in the diet, the results on palmitic acid were the opposite.[90] In the experiments of Hoagland and Snider,[88] increased digestibility coefficients for the least digestible fats were found when the intake was increased.

(d) Mixed Triglycerides vs. Simple Triglycerides. In a well-executed series of experiments, Mattil and Higgins[92] have found that the mixed triglycerides of stearic and oleic acids are more digestible in the rat than corresponding mixtures of the simple triglycerides. Since natural fats contain such mixed triglycerides, it is evident that the results on pure tristearin or tripalmitin may not be of too great importance. These interesting data are summarized in Table 198.

TABLE 198

Digestibility of Stearic Acid Fed as a Simple and as a Mixed Triglyceride[a]

Fat in diet	Fat, grams		Coefficient of digestibility
	In food	In feces	
Tristearin, 10%; triolein, 5%	51.0	29.5	42.2
	79.2	49.4	37.6
Distearomono-olein, 15%	94.2	39.7	57.9
	24.5	9.0	63.3
Tristearin, 5%; triolein, 10%	87.5	27.3	68.7
	35.9	11.3	68.5
Monostearodiolein, 15%	89.4	24.3	72.8
	14.6	3.9	73.3

[a] K. F. Mattil and J. W. Higgins, *J. Nutrition*, **29**, 255–260 (1945).

Up to a melting point of 50° C., there is no progressive lowering in the digestibility of fats with increased melting point. When the melting point exceeds the critical value of approximately 50° C., appreciable amounts of the ingested fat are excreted in the stools.

Although there is reason to believe that such a decline in absorption

[92] K. F. Mattil and J. W. Higgins, *J. Nutrition*, **29**, 255–260 (1945).

may be related to the low digestibility of tristearin, this triglyceride apparently can be largely utilized when fed in natural mixtures whose melting point does not exceed 50° C. In the experiments where blended hydrogenated fats were fed to human subjects, the coefficients of digestibility exceeded 90, even where the completely hydrogenated fat (largely tristearin) comprised as much as 30% of the blend. The satisfactory absorption of the stearic acid in natural oils may be related to the more ready digestibility of the mixed triglycerides.

The extent of digestibility may also be influenced in the rat by the protein content of the diet. Barnes, Primrose, and Burr [93] have reported that a slightly higher digestibility of butter and a lard containing hydrogenated fat was obtained when a high-protein diet was fed than when a diet having a low protein content was administered. However, the digestibility of lard was unchanged on low- and high-protein diets. There are no data as to how widespread the effect of the protein level on fat absorption may be. There is also no information as to whether a similar effect might occur in man.

3. Digestibility of Oleomargarines

There is no reason to suppose that oleomargarines should differ in digestibility from other fats which melt approximately at body temperature. The data recorded in Table 199 indicate that such a hypothesis is well founded and that oleomargarines are well digested.

TABLE 199

Digestibility of Some Oleomargarines

Composition	Number of experiments	Average fat eaten, g.	Coefficient of digestibility
59% oleo oil, 7% lard, 22% vegetable oils (cottonseed, peanut), 12% milk fat[a]	9	—	97.2
41% oleo oil, 32% lard, 24% vegetable oil (peanut), 3% milk fat[a]	7	80	93.4
67% oleo oil, 33% vegetable oil (cottonseed), 0.1% milk fat[a]	4	—	96.8
Vegetable oil, margarine (m.p. 94–95° F. Wiley)[b]	7	86.5	96.7

[a] A. D. Holmes, *Boston Med. Surg. J.*, **192,** 1210–1212 (1925).
[b] H. J. Deuel, Jr., *J. Nutrition*, **32,** 69–72 (1946).

4. Comparison of Digestibility of Fat in Man and Herbivora

From the data already presented, it seems clear that the generally high capacity of man to digest fats is shared by dogs and by rats. For this reason, the experiments on these animals have been used to provide a

[93] R. H. Barnes, M. F. Primrose, and G. O. Burr, *J. Nutrition,* **27,** 179–184 (1944).

further understanding of the factors causing variations in absorption, with the implication that such results are probably applicable to man.

However, the behavior of fats in the herbivora has several variations from man. Some results on herbivores are summarized in Table 200.

TABLE 200

Relative Digestibility of Fats in the Guinea Pig, Rabbit, and Sheep

Fat or oil fed	Guinea pig[a]		Rabbit	Sheep
	Fat in feces, %	Utilization, %	Utilization, %[b]	
Castor	1.25	96.2	92.1	99
Soybean	1.54	94.5	—	—
Olive	1.60	94.5	—	—
Coconut	1.69	94.0	—	—
Salmon	2.03	94.0	—	—
Cod-liver	1.65	93.8	—	—
Neatsfoot	1.64	93.5	—	—
Peanut	2.33	91.8	—	—
Butter	2.58	91.0	—	—
Cottonseed (Wesson oil)	3.36	87.4	91.2	94
Corn	3.35	86.5	—	—
Mutton tallow	5.22	79.8	—	—
Lard	6.70	75.2	—	—
Hydrogenated cottonseed (Crisco)	8.42	73.8	91.0	94
Beef tallow	7.05	72.0	—	—
Oleic acid[b]	—	95.0	—	—
Elaidic acid[b]	—	55.6	—	—

[a] C. M. McCay and H. Paul, *J. Nutrition*, **15**, 377–382 (1938).
[b] H. Paul and C. M. McCay, *Arch. Biochem.*, **1**, 247–253 (1942–1943).

(a) Digestibility of Castor Oil. In marked contrast to the purging action which castor oil exerts in man, it may be readily digested and absorbed by the guinea pig,[94] rabbit,[95] and sheep,[95] and no cathartic action results. Stewart and Sinclair[96] have confirmed the results of the earlier workers in showing that castor oil may be absorbed to the extent of 98% by rats, and that it causes no catharsis. In spite of the very considerable absorption of ricinoleic acid which makes up 85% of the castor oil glycerides, no evidence for the presence of ricinoleic acid in the phospholipids of the small intestine, liver, or muscle, or in the liver glycerides was found. Stewart and Sinclair believe that this indicates that the hydroxy acid is capable of rapid metabolism.

(b) Coefficient of Digestibility for Common Food Fats. The digestibility of cottonseed oil and hydrogenated cottonseed oil do not differ greatly in the rabbit and sheep from the value in the human subject. However, practically all fats have a considerably lower utilization in the

[94] C. M. McCay and H. Paul, *J. Nutrition*, **15**, 377–382 (1938).
[95] H. Paul and C. M. McCay, *Arch. Biochem.*, **1**, 247–253 (1942–1943).
[96] W. C. Stewart and R. G. Sinclair, *Arch. Biochem.*, **8**, 7–11 (1945).

guinea pig than in other species. This decrease is not only noted for the high-melting fats, but also for such normally well-absorbed products as corn oil and lard. McCay and Paul [94] believe that the guinea pig is especially sensitive to the melting point of the fat.

(c) Comparison of Utilization of Oleic and Elaidic Acid. Whereas the rat can utilize oleic acid and its geometrical isomer, elaidic acid, equally well (95.4 and 95.6%, respectively),[95] the guinea pig utilizes only 55.6% of the elaidic acid as compared with 94.6 and 95.4% digestibility determined for oleic acid. Elaidic acid is one of the "iso" acids formed in the hydrogenation of fats containing linoleic acid.

B. Rate of Absorption from Gastro-intestinal Tract

The speed at which fat can be removed from the intestine offers another satisfactory means for evaluation of its nutritive value. It is conceivable that two fats may have a marked difference in rate of disappearance from the intestine, despite the fact that when taken in moderate amounts they eventually are both practically completely digested. The maximum quantity of these fats which could be utilized without digestive disturbances would vary; diarrhea would be expected to occur more readily with the more slowly absorbed fat; the total utilization possible over a given time would therefore become a function of the rapidity with which a disposition of the ingested fat could be made.

Unfortunately, the data on relative rates of fat absorption are considerably limited. The paucity of information is partly a result of the inadequacy of the procedures available for study. The intestinal loop method is far from physiological, especially since pancreatic and hepatic secretions are usually excluded from the loop. Although the indirect method, which involves the determination of the rate of increase in blood lipids or of the fat in thoracic lymph, gives some information about fat absorption, the results are not sufficiently precise to be considered quantitative. The most satisfactory results have been obtained by removal of the gastro-intestinal tract with its contents at various periods after the feeding of fat and determining the fat residue remaining in the intestine. Such a procedure has been employed by Irwin, Steenbock, and Templin,[97] and this method has been modified by Deuel, Hallman, and Quon.[98] It was found that fat absorption is not affected by age in the range four to seven months, or by sex, pregnancy, or season.[97]

1. Units for Expressing Rate of Absorption

The best method for making comparisons in the rate of absorption of different fats would appear to be on the basis of the body surface area. This basis for comparison of physiological response is not limited to its

[97] M. H. Irwin, H. Steenbock, and V. M. Templin, *J. Nutrition,* **12,** 85–101 (1936).
[98] H. J. Deuel, Jr., L. F. Hallman, and S. Quon, *J. Biol. Chem.,* **128,** xix (1939).

well-known application to basal metabolism, but it has been shown to be the most satisfactory method for evaluation of the absorption of glucose.[99] It is also known that a proportionality exists between the body surface area and the area of the intestine. Since the rate of absorption must be a function of the available surface of the small intestine, it is logical that any biometric measurement related to this value would be useful in the correlation of such data.

Steenbock, Irwin, and Weber [100] have referred absorption to the proportion of ingested fat which has disappeared in a given time. It is obvious that such a figure depends not only on the absolute amount of fat absorbed, but also on the size of the dose administered. It is equally obvious that this value would vary as well with the size of the animal being tested. Deuel, Hallman, and Leonard,[101] in an analysis of these factors, have

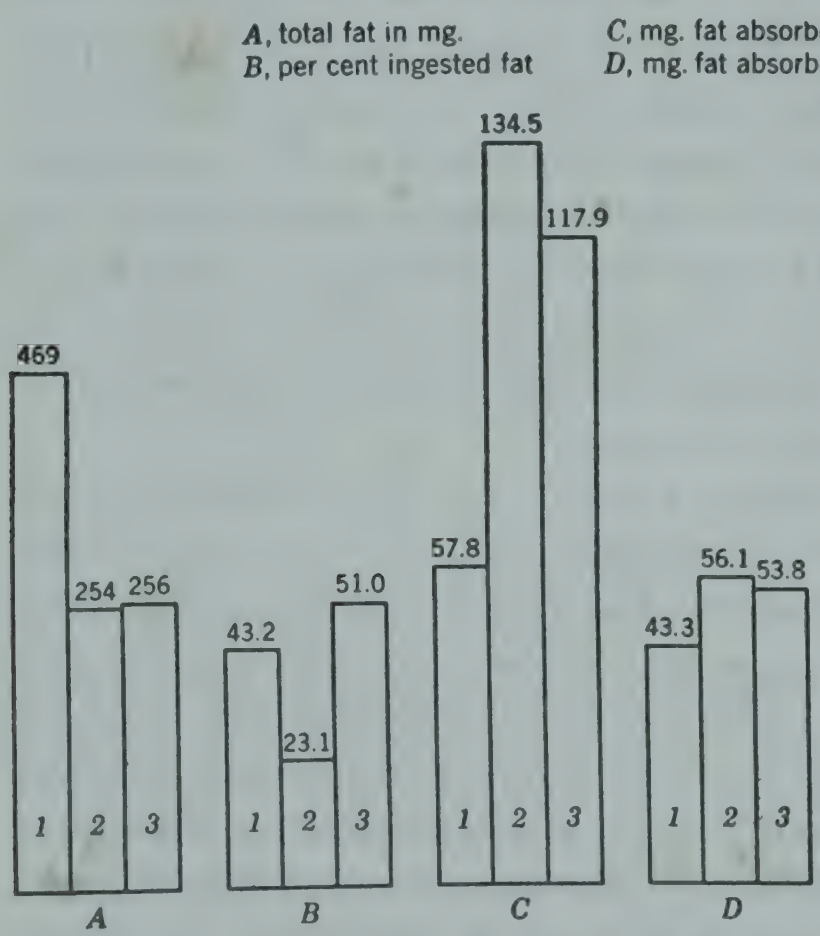


Fig. 193. Comparison of the different methods of expressing absorption in male rats (fed margarine fat).



Fig. 194. Different methods of expressing absorption in female rats (fed margarine fat).

concluded that surface area offers the most satisfactory method for interpretation of the rate of absorption. Figures 193 and 194 and the table on page 787 give a comparison between these two methods.

2. Comparative Absorption Rates of Some Common Fats

According to the results of Steenbock, Irwin and Weber,[100] considerable variations may be obtained in the absorption rate of different vegetable

[99] E. M. MacKay and H. C. Bergman, *J. Biol. Chem.*, **101,** 453–462 (1933).
[100] H. Steenbock, M. H. Irwin, and J. Weber, *J. Nutrition*, **12,** 103–111 (1936).
[101] H. J. Deuel, Jr., L. Hallman, and A. Leonard, *J. Nutrition*, **20,** 215–226 (1940).

and animal fats from the gastro-intestinal tract of the rat. These authors have arranged the fats and oils in the following order based on the percentage of ingested fat which was absorbed in a four-hour period: butter (oil), 71.0; halibut liver, 70.2; cod liver, 67.7; raw linseed, 67.0; olive, 63.4; lard, 57.0; rancid lard, 53.8; commercial shortening A, 53.8; cottonseed, 53.7; commercial shortening B, 52.8; cocoa butter, 47.9; coconut, 47.4; palm, 37.4; and oleo stock, 35.8. The interpretation of these experiments might be improved if they had been based on surface area.

On the other hand, Deuel, Hallman, and Leonard [101] concluded that no significant differences exist in the rate of absorption of butterfat, margarine (hydrogenated cottonseed oil), cottonseed oil, or coconut oil, although rapeseed oil was more slowly absorbed than other common oils. The following absorptions (in milligrams per 100 square centimeters per hour) were found in three- and six-hour experiments, respectively: margarine fat, 44.5, 46.1; butterfat, 49.6, 42.1; cottonseed oil, 39.8, 39.8; coconut oil, 42.0, 43.2; and rapeseed oil, 38.5, 30.0.

Group	Number of rats	Weight, g.	Surface area, sq. cm.	Fat fed, mg.
Male				
1	33	270	360	1087
2	19	65	153	1101
3	15	74	165	502
Female				
4	9	150	253	391
5	16	64	150	300

3. Absorption of Short-Chain Triglycerides

It is important also to consider the absorption rate of short-chain triglycerides, inasmuch as these make up an appreciable proportion of butter and coconut oil molecules. In a study of a number of synthetic triglycerides, Deuel and Hallman [102] found that the shortest-chain component, triacetin, was most rapidly absorbed and that absorption becomes progressively slower with lengthening of the chain. The values found were as follows (mg. per 100 sq. cm. per hr.): triacetin (C_2), 68.1; tributyrin (C_4), 65.0; tri-isovalerin, 45.7; tricaproin (C_6), 54.5; tricaprylin (C_8), 45.9; and trilaurin (C_{12}), 21.9.

4. Absorption of Odd-Chain Triglycerides

Coupled with the observations on the variations in absorption rate with chain length is the interesting finding that the triglycerides composed of odd-chain acids are more slowly absorbed than the corresponding ones

[102] H. J. Deuel, Jr., and L. Hallman, *J. Nutrition*, **20**, 227–232 (1940).

composed of even-chain acids. The figures found for tripropionin (C_3), 31.4, trivalerin (C_5), 32.9, and triheptylin (C_7), 28.0, are approximately 50% of those of the triglycerides composed of even-chain fatty acids of similar length. These variations are to be ascribed to differences in the rate of absorption of the component fatty acids rather than in the rate of hydrolysis.[103] Triglycerides composed of odd-chain acids are not found in any natural fats or oils.

5. Effect of Adrenal Cortex on Absorption

In discussing the nutritive value of fat, one should consider the role of the adrenocortical hormones, because their effect on absorption might vary with the different fats. Verzár and Laszt [104, 105] have demonstrated that the speed of fat absorption is markedly lower in rats following adrenalectomy.

This lowering of fat absorption was confirmed by Bavetta *et al.*[106] and shown to be a primary effect, since it still occurred in adrenalectomized animals in which concentration of the blood was prevented by treatment with salt. Moreover, it was associated with a slower rate of absorption of fatty acid since the rate of lipolysis was not decreased. Although Barnes *et al.*[107] failed to observe an inhibitory effect of adrenalectomy on absorption of corn oil, they subsequently reported a lowering in the absorption rate of emulsified hydrogenated cottonseed oil.[108]

A possible variation in the effect of adrenalectomy on fat absorption is to be noted in the demonstration by Bavetta and Deuel [109] that adrenalectomy did not alter the rate of absorption of sodium butyrate or its triglyceride. In a later study, Bavetta[110] found that there was no alteration in absorption of other triglycerides having water-soluble fatty acids (tricaproin and tricaprylin), but in the case of tricaprin, which gives rise on hydrolysis to the water-insoluble acid, capric, a variation in absorption was obtained. It would seem questionable whether coconut oil and butter contain a significantly large proportion of the short-chain fatty acids to make them suitable dietary fats to be used in adrenal deficiency. Moreover, the cortical hormones which are capable of relieving the other deficiency symptoms in Addison's disease (disease of the adrenal cortex) also restore the fat absorption to normal.[106] Figure 195 gives a graphic comparison of the fat absorption in normal and adrenalectomized rats.

[103] H. J. Deuel, Jr., L. Hallman, and A. Reifman, *J. Nutrition*, **21**, 373–382 (1941).
[104] F. Verzár and L. Laszt, *Biochem. Z.*, **276**, 11–16 (1935).
[105] F. Verzár and L. Laszt, *Biochem. Z.*, **278**, 396–400 (1935).
[106] L. Bavetta, L. Hallman, H. J. Deuel, Jr., and P. O. Greeley, *Am. J. Physiol.*, **134**, 619–622 (1941).
[107] R. H. Barnes, E. S. Miller, and G. O. Burr, *J. Biol. Chem.*, **140**, 241–253 (1941).
[108] R. H. Barnes, I. I. Rusoff, and G. O. Burr, *Proc. Soc. Exptl. Biol. Med.*, **49**, 84–87 (1942).
[109] L. Bavetta and H. J. Deuel, Jr., *Am. J. Physiol.*, **136**, 712–715 (1942).
[110] L. Bavetta, *Am. J. Physiol.*, **140**, 44–46 (1943).

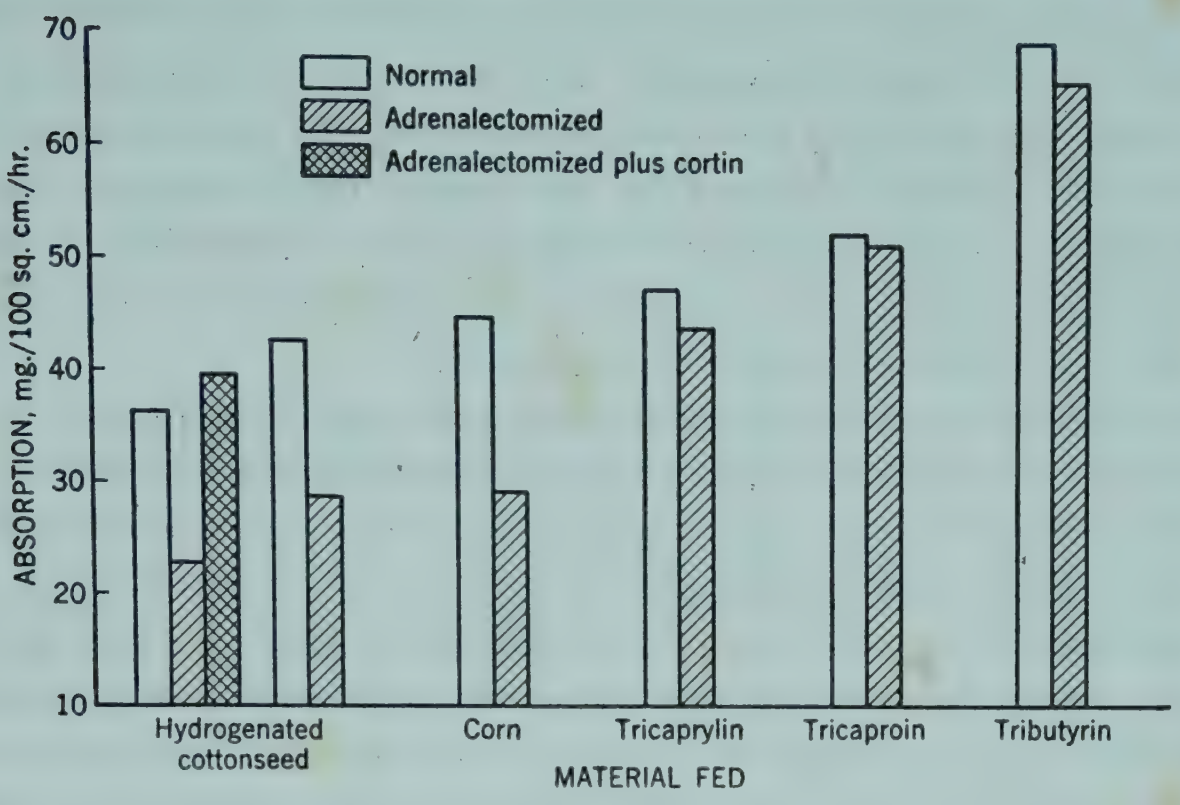


Fig. 195. Comparative rates of absorption of hydrogenated cottonseed oil (a margarine fat), corn oil, tricaprylin, tricaproin, and tributyrin in normal and adrenalectomized rats, and of hydrogenated cottonseed oil in adrenalectomized, cortin-treated rats.

C. Intermediary Metabolism

There are no marked differences in the intermediary metabolism of the various naturally occurring animal and vegetable fats. The fats in the tissues originate not only from the fat ingested, but also from carbohydrates and protein in the diet. With diets in which the proportion of any one foodstuff is not too one-sided and in which unusual fats are not present in too great amounts, the composition of the deposited fat is fairly uniform for any species of animal. However, there are certain conditions under which the ingested fat may markedly alter the type of fat deposited. The present discussion will be limited to those phases of intermediary metabolism in which variations may be expected as a result of the dietary fat. For a more complete discussion of the general subject of intermediary fat metabolism, the reader is referred to the excellent recent review of Stadie.[111]

1. Deposition of Ingested Fat in Tissues

There are certain fats which can not be deposited in the tissues irrespective of the amount which is ingested. This was shown by Eckstein [112, 113] to be the case in the ingestion of tributyrin and tricaproin, although the fat deposited differed somewhat from that obtained on fat-free diets. Morehouse,[114] working with deuteriotributyrin, could find no evidence for

[111] W. C. Stadie, *Physiol. Revs.*, **25,** 395–441 (1945).
[112] H. C. Eckstein, *J. Biol. Chem.*, **81,** 613–628 (1929).
[113] H. C. Eckstein, *J. Biol. Chem.*, **84,** 353–357 (1929).
[114] M. G. Morehouse, *J. Biol. Chem.*, **155,** 33–38 (1944).

the storage of the butyric acid in the deposit fat of rats or of its transformation to the longer chain acids. Her data were interpreted to indicate that the butyric acid was not recombined with glycerol after absorption, but that it was rapidly utilized for the production of energy. Only traces of tricaprylin can be deposited,[115] but Powell [116] was able to produce a depot fat in rats which contained 15% of tricaprin when this triglyceride comprised an important proportion of the diet.

On the other hand, certain fatty acids normally not present in deposit fat will be found there if an excess of that particular component is present in the diet. Munk [117] was able to demonstrate the presence of triglycerides containing erucic acid ($C_{22}H_{42}O_2$) in dog fat after rapeseed oil was fed to the previously starved animal. Glycerides of lauric [115] and myristic [113] acids have been reported in rat fat after triglycerides containing these acids made up an appreciable proportion of the diet. Arachidic acid has been obtained in the fat of hogs fed large amounts of peanuts,[118] although this fatty acid had been previously found almost exclusively in peanut oil. Ellis and co-workers [118–122] have shown that hog fat may be markedly softened by diets containing corn, peanut, or soybean oil, whereas cottonseed oil had a tendency to produce more solid fat. Anderson and Mendel [123] have also exhaustively studied this problem on rats. They found that the resulting body fat reflected the composition of the food fat when cottonseed, peanut or soybean oil was fed, while with coconut oil or butterfat, the deposited fat differed considerably. The hardest fat (*i.e.*, that with the highest melting point) was found when a high-carbohydrate diet was fed. The linoleic acid content of egg-yolk fat [124] and of pig depot fat [119, 125] is also proportional to the amount of this essential fatty acid in the diet. Appel *et al.*[126] have made the remarkable discovery that male goats are able to store odd-chain acids from C_{13} to C_{17} to the extent of 33% of the total body fat after the animals are fed on a fat mixture containing largely C_{10} to C_{23} odd-chained acids. The digestibility was found to be 79%. When coconut oil was used, the digestibility was 91%, and the shortest chain acids stored were C_{12}. Visscher [126a] has also been able to separate undecylic (hendecanoic) acid (C_{11}) in an amount of 24% of the depot fat

[115] M. Powell, *J. Biol. Chem.*, **89,** 547–552 (1930).
[116] M. Powell, *J. Biol. Chem.*, **95,** 43–45 (1932).
[117] I. Munk, *Arch. path. Anat. Virchow's*, **95,** 407–467 (1884).
[118] N. R. Ellis and H. S. Isbell, *J. Biol. Chem.*, **69,** 239–248 (1926).
[119] N. R. Ellis and J. H. Zeller, *J. Biol. Chem.*, **89,** 185–197 (1930).
[120] N. R. Ellis, C. S. Rothwell, and W. O. Pool, *J. Biol. Chem.*, **92,** 385–398 (1931).
[121] N. R. Ellis and H. S. Isbell, *J. Biol. Chem.*, **69,** 219–238 (1926).
[122] N. R. Ellis and O. G. Hankins, *J. Biol. Chem.*, **66,** 101–122 (1925).
[123] W. E. Anderson and L. B. Mendel, *J. Biol. Chem.*, **76,** 729–747 (1928).
[124] E. M. Cruickshank, *Biochem. J.*, **28,** 965–977 (1934).
[125] G. Collin, T. P. Hilditch, and C. H. Lea, *J. Soc. Chem. Ind.*, **48,** 46–50T (1929).
[126] H. Appel, H. Böhn, W. Keil, and G. Schiller, *Z. physiol. Chem.*, **274,** 186–205 (1942).
[126a] F. E. Visscher, *J. Biol. Chem.*, **162,** 129–132 (1946).

of young rats fed on the triglyceride composed of this fatty acid for 6 weeks.

2. Carbohydrate Formation from Fats

In spite of the fact that glycerol itself is completely transformable to glycogen,[127] none of the natural fats under normal conditions can be shown to give rise to appreciable amounts of carbohydrate in the animal body. This is presumably because the glycerol moiety is recombined with the fatty acids after absorption enabling the fatty material to be reconverted to neutral fats before storage occurs or further intermediary changes take place. Only after feeding of these triglycerides, which cannot be stored (and probably not resynthesized in the body), can an appreciable accumulation of glycogen be noted.[128] Thus, when triacetin, tributyrin, tricaproin or tricaprylin was fed, an increase in liver glycogen could be shown which was equal to that produced by isomolecular quantities of glycerol. When triglycerides composed of the shorter odd-chain fatty acids were fed, even larger amounts of glycogen were found. Here it was shown that the glycogen arose not alone from the glycerol moiety but also from the fatty acid portion of the diet. The sodium salts of the odd-chain fatty acids or, in some cases, their ethyl esters were found to be convertible to carbohydrate in proportion to their ability to be transformed to propionic acid.[129, 130]

In spite of the glycogenic capacity of the short-chain triglycerides, it has not been possible to demonstrate that these acids afford a ready source of available carbohydrate after such natural fats as butter or coconut oil are fed. This is presumably to be traced to the relatively insignificant role, from a quantitative standpoint, that such triglycerides play. No natural fats contain significant amounts of the odd-chain fatty acids. Therefore, in spite of their marked effectiveness as sources of carbohydrate, this fact is of no practical importance insofar as our usual food fats are concerned. The interrelations of fat and carbohydrate are discussed more completely elsewhere.[12]

3. Ketone Body Formation after Oxidation of Fats

All even-chain fatty acids when fed to fasting rats as their sodium salts [131] or their ethyl esters [132] have been shown to give rise to the so-

[127] W. H. Chambers and H. J. Deuel, Jr., *J. Biol. Chem.*, **65,** 21–29 (1925).
[128] H. J. Deuel, Jr., J. S. Butts, H. Blunden, C H. Cutler, and L. Knott, *J. Biol. Chem.*, **117,** 119–129 (1937).
[129] H. J. Deuel, Jr., J. S. Butts, L. F. Hallman, and C. H. Cutler, *J. Biol. Chem.*, **112,** 15–23 (1935).
[130] J. S. Butts, H. Blunden, W. Goodwin, and H. J. Deuel, Jr., *J. Biol. Chem.*, **117,** 131–133 (1937).
[131] J. S. Butts, C. H. Cutler, L. F. Hallman, and H. J. Deuel, Jr., *J. Biol. Chem.*, **109,** 597–613 (1935).
[132] H. J. Deuel, Jr., L. F. Hallman, J. S. Butts, and S. Murray, *J. Biol. Chem.*, **116,** 621–639 (1936).

called ketone bodies, *i.e.*, diacetic acid (CH_3COCH_2COOH), β-hydroxybutyric acid ($CH_3CHOHCH_2COOH$), and acetone (CH_3COCH_3). On the other hand, there is some evidence that, although the odd-chain fatty acids give rise to no ketonuria (ketone bodies in the urine),[132] some of the higher ones (but not propionic acid) may give a slight ketonemia (ketone bodies in the blood).[133] However, Krainick [134] has recently obtained negative evidence that a ketonemia occurs when odd-chain acids are fed. There is no evidence that different natural fats show any variations in their capability to produce ketone bodies under suitable conditions. For a further discussion of this subject the reader is referred to the review written by Deuel and Morehouse.[12]

D. Sparing Action of Fat on Vitamin Requirements

The time that an animal may survive on a thiamin-free diet has been shown to be related to the nature of the diet. On a high-carbohydrate diet, the survival period is considerably shortened, presumably due to the more rapid utilization of the thiamin for the manufacture of cocarboxylase or to the greater requirement for cocarboxylase. This coenzyme is required for the metabolism of pyruvic acid; this keto acid originates as an intermediate in the metabolism of carbohydrate, but not in the breakdown of fat. When animals are placed on a high-carbohydrate, low-thiamin diet, they will frequently circumvent the approaching polyneuritis by limiting the carbohydrate intake by fasting.

1. Effect of Fat on Thiamin Requirement

The rationale for observations on the relation of diet to susceptibility to polyneuritis has been firmly established by Evans and Lepkovsky.[135, 136] These workers found that, on diets adequate except in vitamin B_1 content, the onset of polyneuritis was markedly retarded on high-fat diets. This so-called "vitamin B_1 sparing action" was noted with all fats studied (lard, coconut oil, partially hydrogenated cottonseed oil (Crisco), cottonseed oil, butter, and walnut oil), except certain fats with high melting points (hydrogenated perilla oil, m.p. 67.5° C) whose absorption was poor.[137] Certain of the purified triglycerides, such as trimyristin and tricaprylin, were found to be very effective, while tristearin was ineffective.[138] Salmon and Goodman [139] also reported that numerous synthetic esters of the fatty acids were active, with the maximum sparing

[133] E. M. MacKay, A. N. Wick, and C. P. Barnum, *J. Biol. Chem.*, **136,** 503–507 (1940).
[134] H. G. Krainick, *Klin. Wochschr.*, **19,** 803–808 (1940).
[135] H. M. Evans and S. Lepkovsky, *Science,* **68,** 298 (1928).
[136] H. M. Evans and S. Lepkovsky, *J. Biol. Chem.*, **83,** 269–287 (1929).
[137] H. M. Evans and S. Lepkovsky, *J. Biol. Chem.*, **96,** 165–177 (1932).
[138] H. M. Evans and S. Lepkovsky, *J. Biol. Chem.*, **96,** 179–188 (1932).
[139] W. D. Salmon and J. G. Goodman, *J. Nutrition*, **13,** 477–500 (1937).

action being found with the eight-carbon fatty acid. Stirn, Arnold, and Elvehjem [140] also confirmed the observation that tricaproin and triacetin exert a thiamin sparing action. The sparing action apparently is not caused by any interaction between the fat and thiamin in the intestine, since it was also observed when the vitamin was administered parenterally.[141] Coconut oil has been reported to be the most effective fat in sparing vitamin B_1, [139, 142] followed in order by lard, Crisco, butterfat, synthetic lard, cottonseed oil, corn oil, olive oil, hydrogenated sesame oil, and sesame oil.[142]

2. Effect of Fat on Requirement for Riboflavin

Evans and co-workers [143] found that fat had no sparing action on the requirement for riboflavin (vitamin B_2). In fact, Mannering, Lipton, and Elvehjem [144] have postulated that the riboflavin requirement of rats is increased on high-fat diets. This is possibly because of the reduced ability of animals on such diets to produce this vitamin by the normal method of bacterial synthesis in the intestine. Confirmatory experiments are also reported by Mannering, Orsini, and Elvehjem.[145] Lard was the only fat studied by these workers, although it was later stated that all fats function equally in increasing the riboflavin requirement.[146] The results on puppies, on the other hand, fail to indicate a similar increase in riboflavin requirement with high-fat diets.[147]

3. Relationship of Unsaturated Fatty Acids to Pyridoxine Requirement

The acrodynia, which is generally considered to be a symptom of pyridoxine (B_6) deficiency, can not be produced when a sufficient amount of linoleic acid is available. It has been demonstrated that pyridoxine, pantothenic acid, and the unsaturated fatty acids are all required jointly for sustained growth in rats, but they did not completely cure the scaly condition of the tail and hind paws although they alleviated the acrodynia. Possibly, a fourth factor also is required for the cure of the skin lesions.[148]

[140] F. E. Stirn, A. Arnold, and C. A. Elvehjem, *J. Nutrition,* **17,** 485–495 (1939).
[141] H. M. Evans and S. Lepkovsky, *J. Biol. Chem.,* **99,** 235–236 (1932).
[142] H. M. Evans, S. Lepkovsky, and E. A. Murphy, *J. Biol. Chem.,* **107,** 439–442 (1934).
[143] H. M. Evans, S. Lepkovsky, and E. A. Murphy, *J. Biol. Chem.,* **107,** 443–447 (1934).
[144] G. J. Mannering, M. A. Lipton, and C. A. Elvehjem, *Proc. Soc. Exptl. Biol. Med.,* **46,** 100–104 (1941).
[145] G. J. Mannering, D. Orsini, and C. A. Elvehjem, *J. Nutrition,* **28,** 141–156 (1944).
[146] Council on Foods and Nutrition of the American Medical Association, *J. Am. Med. Assoc.,* **119,** 1425–1427 (1942).
[147] R. L. Potter, A. E. Axelrod, and C. A. Elvehjem, *J. Nutrition,* **24,** 449–460 (1942).
[148] F. W. Quackenbush, H. Steenbock, F. A. Kümmerow, and B. R. Platz, *J. Nutrition,* **24,** 225–234 (1942).

4. Sparing Action of Fat on Other Vitamins

An increase in dietary fat has a slight sparing effect on the biotin requirement,[149, 150] as well as on that of pantothenic acid.[151] A sparing action on vitamin A has also been noted.[152] This may result either from the improvement in absorption of vitamin A,[153] or from the synergistic effect of the tocopherol present in the fat on the vitamin A and especially on the carotene utilization.[65, 66, 154]

E. Prophylactic and Curative Action of Fat on Deficiency Symptoms Resulting from a Fat-Free Diet

Although Osborne and Mendel stated[155] in 1920 that "if true fats are essential for nutrition during growth, the minimum necessary must be exceedingly small," it was later found in the Yale laboratories that better growth was obtained in rats receiving adequate fat-soluble vitamins when fats were also present in the diet.[156]

The first definite proof of a fat-deficiency disease which results from rigid exclusion of fat from the diet was demonstrated by Evans and Burr,[157] and later by Burr and Burr.[158] The symptoms are a scaly skin, particularly with an incrustation of the tail (Fig. 196), a marked retardation in growth followed by a loss in weight, kidney lesions with an attendant hematuria, and finally death.[5, 6] Sterility also develops in the male; poor ovulation, an impaired reproduction and lactation result in the female; a high water consumption is usually observed, and an excessively high R.Q. and basal metabolism are accompanying phenomena.[159] The inability of some workers to elicit the fat-deficiency disease on ether-extracted diets in which corn or rice starch is the main component has been shown[160] to be traceable to the 0.5% of unextractable fatty acids (largely linoleic acid) combined with the starch. Potato starch has phosphoric acid rather than fatty acids combined with it.[161]

[149] E. M. MacKay and R. H. Barnes, *Proc. Soc. Exptl. Biol. Med.*, **46,** 353–357 (1941).
[150] E. Nielsen and C. A. Elvehjem, *J. Biol. Chem.*, **144,** 405–409 (1942).
[151] G. O. Burr, in M. G. Wohl, *Dietotherapy,* Saunders, Philadelphia, 1945. p. 78.
[152] R. A. Dutcher, P. L. Harris, E. A. Hartzler, and N. B. Guerrant, *J. Nutrition,* **8,** 269–283 (1934).
[153] K. D. Muelder and E. Kelly, *J. Nutrition,* **23,** 335–344 (1942).
[154] G. L. Martin, *J. Nutrition,* **17,** 127–141 (1939).
[155] T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, **45,** 145–152 (1920–1921).
[156] A. J. McAmis, W. E. Anderson, and L. B. Mendel, *J. Biol. Chem.*, **82,** 247–262 (1929).
[157] H. M. Evans and G. O. Burr, *Proc. Soc. Exptl. Biol. Med.*, **24,** 740–743 (1926–1927).
[158] G. O. Burr and M. M. Burr, *J. Biol. Chem.*, **82,** 345–367 (1929).
[159] L. G. Wesson and G. O. Burr, *J. Biol. Chem.*, **91,** 525–539 (1931).
[160] H. M. Evans and S. Lepkovsky, *J. Biol. Chem.*, **96,** 143–156 (1932).
[161] T. C. Taylor and H. A. Iddles, *Ind. Eng. Chem.*, **18,** 713–717 (1929).

1. The Effective Principle in Curing the Fat-Deficiency Disease of Rats

Burr and Burr [158] found that corn oil was especially efficient in curing fat deficiency, whereas butterfat was very poor, and coconut oil possessed practically no ability in this respect. The effective principle was found to be a fatty acid; glycerol and the nonsaponifiable fraction both gave completely negative results. The saturated fatty acids, as well as oleic acid, were found to be without curative effect. Linoleic acid [158, 162] and arachidonic acid [47–50] were found to be the essential acids of highest activity, while linolenic acid has a somewhat lower potency.[162] The effectiveness of



Fig. 196. The scaly skin of a rat produced by feeding a diet very low in fat.[161a]

the natural fats in preventing the fat-deficiency disease must be in proportion to their content of these essential acids (see Tables 190 and 191). Linoleyl alcohol,[49] docosahexenoic acid,[6] and hexahydroxystearic acid,[163] complete the list of the compounds which have been shown to be active. However, many unsaturated fatty acids have been found to be inactive. Not only oleic acid,[158, 160] but its geometric isomer, elaidic acid,[164] belong in this category. Other acids that proved to be useless in curing the fat-deficiency disease are erucic and ricinoleic,[49] linolelaidic and $\Delta^{9,11}$-octadecadienoic,[165] α-elaeostearic,[162] dioxidostearic, trihydroxystearic, tetrahydroxystearic, and chaulmoogric acids,[163] and also clupanodonic acid.[166]

[161a] M. G. Wohl, *Dietotherapy,* Saunders, Philadelphia, 1945.
[162] G. O. Burr, M. M. Burr, and E. S. Miller, *J. Biol. Chem.,* **97,** 1–9 (1932).
[163] E. M. Hume, L. C. A. Nunn, I. Smedley-Maclean, and H. H. Smith, *Biochem. J.,* **32,** 2162–2177 (1938).
[164] R. G. Sinclair, *J. Nutrition,* **19,** 131–140 (1940).
[165] G. O. Burr, in *Chemistry and Medicine,* Univ. Minnesota Press, 1940, p. 101.
[166] U. Tange, *Sci. Papers Inst. Phys. Chem. Research Tokyo,* **20,** 13–28 (1932).

A number of workers[122, 167, 168] have shown that the amount of the essential fatty acids in animal tissue fats is directly dependent on the content in the diet and that no synthesis occurs *in vivo*. This is further supported by the demonstration of Schoenheimer and Rittenberg[169] that no exchange of hydrogen with deuterium is possible in the essential acids.

The capabilities of a substance to produce growth and to cure the scaly condition do not always coincide. Linoleic acid and (to a lesser extent) arachidonic acid accomplish both these results. These acids also lower the water consumption to normal, and this reaction always seems to be associated with the cure of the skin condition. Linolenic acid and the esters of cod-liver oil acids induce growth without improving the skin condition or lowering the abnormally high water consumption. However, all compounds which cure the skin condition induce growth.[6] It has been suggested that the growth effects and the cure of the dermatitis may not necessarily be interrelated. There is a lowering in fat absorption in the fat-deficiency disease, but this is possibly due to the poor condition of the animals rather than being a specific effect of the disease.[170]

2. Fat-Deficiency Disease in Animals Other Than Man

Although understanding of the essential fatty acid story has been largely learned from experiments on rats, mice are also susceptible to the deficiency.[171] The failure to demonstrate the dietary deficiency in chickens by Russell, Taylor, and Polskin[172] may have been due to the presence of cornstarch in the diet. Although the external deficiency symptoms have not been demonstrated in hogs, a striking decrease in the linoleic acid content of the depot fat occurs following a prolonged fat-free diet.[122] The dog is readily susceptible to the deficiency.[173]

3. Fat-Deficiency Disease in Man

Although one would hardly expect to find the more serious symptoms observed in rats, after subjection of human subjects to rigidly controlled fat-free diets, certain types of eczema in man undoubtedly are the result of a fat deficiency. Several workers have reported in infants on fat-free diets an eczema which was readily cured by fat feeding.[174, 175] The eczematous condition is usually accompanied by a lowering in serum linoleate

[167] A. Banks, T. P. Hilditch, and E. C. Jones, *Biochem. J.*, **27,** 1375–1382 (1933).
[168] H. E. Longenecker, *J. Biol. Chem.*, **128,** 645–658 (1939).
[169] R. Schoenheimer and D. Rittenberg, *Physiol. Revs.*, **20,** 218–248 (1940).
[170] R. H. Barnes, E. S. Miller, and G. O. Burr, *J. Biol. Chem.*, **140,** 773–778 (1941).
[171] E. A. White, J. R. Foy, and L. R. Cerecedo, *Proc. Soc. Exptl. Biol. Med.*, **54,** 301–302 (1943).
[172] W. C. Russell, M. W. Taylor, and L. J. Polskin, *J. Nutrition*, **19,** 555–562 (1940).
[173] A. E. Hansen and H. F. Wiese, *Proc. Soc. Exptl. Biol. Med.*, **52,** 205–208 (1943).
[174] F. von Gröer, *Biochem. Z.*, **97,** 311–329 (1919).
[175] A. E. Hansen, *Am. J. Diseases Children*, **53,** 933–946 (1937).

and arachidonate,[176-178] as well as a drop of about 25% in the iodine number of the blood serum lipids.[178] The cure occurs with a concomitant rise in linoleate but not in arachidonate.[179] Some workers have failed to show a relationhips of the essential fatty acids to eczema,[180, 181] but here it may be assumed that an eczema of a different type may have been studied. A



Fig. 197. Picture at the left is that of a six-month-old infant who had had a very resistant eczema since 2½ months of age. At the right is a picture of the same child six months after lard was included in the diet.[161a]

lowering in the iodine number of the blood serum lipids of rats has been shown to occur concomitantly with the scaly condition of the skin resulting from a fat-free diet.[182] The only result of a prolonged fat-low diet in the case of an adult human subject over a six-month period was a 50% reduction in arachidonic and linoleic acids of the serum; the subject remained in good health.[183] Figure 197 shows a six-month-old infant before and after eczema was cured by the inclusion of lard in the diet.

[176] W. R. Brown and A. E. Hansen, *Proc. Soc. Exptl. Biol. Med.*, **36,** 113–117 (1937).
[177] H. K. Faber and D. B. Roberts, *J. Pediatrics,* **6,** 490–493 (1935).
[178] T. Cornbleet, *Arch. Dermatol. Syphilol.,* **31,** 224–226 (1935).
[179] C. W. Finnerud, R. L. Kesler, and H. F. Wiese, *Arch. Dermatol. Syphilol.,* **44,** 849–861 (1941).
[180] S. J. Taub and S. J. Zakon, *J. Am. Med. Assoc.,* **105,** 1675 (1935).
[181] J. E. Ginsberg, C. Bernstein, Jr., and L. V. Job, *Arch. Dermatol. Syphilol.,* **36,** 1033–1038 (1932).
[182] A. E. Hansen and G. O. Burr, *Proc. Soc. Exptl. Biol. Med.,* **30,** 1201–1203 (1933).
[183] W. R. Brown, A. E. Hansen, G. O. Burr, and I. McQuarrie, *J. Nutrition,* **16,** 511–524 (1938).

F. Comparative Effects of Various Fats in Promoting Growth

The ability of a nutrient to afford growth has been widely accepted as an index of its nutritive value. If any single essential component is absent from the diet, growth will not take place and nutritional failure and death will eventually result.

1. Results on Normal Rats

Although it is known that better growth will occur when fat is available in the diet than with a fat-free regimen, it is generally considered that all digestible fats can supply the fat requirement equally well, provided, of course, that the need for the fat-soluble vitamins and for the unsaturated fatty acids has been met. However, it has recently been claimed that fats show a qualitative difference in supporting growth of young rats. Schantz, Elvehjem, and Hart [184] reported that young rats grew best over the first six weeks after weaning on a diet of skimmed milk, homogenized with butterfat. When corn oil, coconut oil, cottonseed oil, or soybean oil was used in place of the butterfat, growth was markedly inferior, although the differences between the diets largely disappeared after six weeks. It was later reported [185] that the saturated acid fraction of butter produced a growth rate superior to that of the whole butter, although the volatile fraction was ineffective and the unsaturated residue was largely ineffective until it was hydrogenated.[186] These data led Schantz *et al.* to the conclusion that certain saturated long-chain acids which are present in butter, but not in the other fats tested, were responsible for the improved growth; it was also believed that the long-chain unsaturated acid or acids in butter were rendered particularly effective by hydrogenation. On the other hand, two different groups of investigators have recently failed to confirm the fact that the saturated fatty acid fraction of butter has any specific effect on growth.[187, 188]

The results obtained by Deuel and associates [189] on whole butter have been diametrically opposed to those of the Wisconsin [184–186] investigators. In the experiments conducted by the former group, the liquid skimmed milk in the diet was replaced by skimmed milk powder and the fats to be tested were added in the proportion found in whole milk powder, *i.e.*,

[184] E. J. Schantz, C. A. Elvehjem, and E. B. Hart, *J. Dairy Sci.*, **23,** 181–189 (1940).
[185] E. J. Schantz, R. K. Boutwell, C. A. Elvehjem, and E. B. Hart, *J. Dairy Sci.*, **23,** 1205–1210 (1941).
[186] R. K. Boutwell, R. P. Geyer, C. A. Elvehjem, and E. B. Hart, *J. Dairy Sci.*, **24,** 1027–1034 (1941).
[187] K. M. Henry, S. K. Kon, T. P. Hilditch, and M. L. Meara, *J. Dairy Research*, **14,** 45–54 (1945).
[188] E. L. Jack, J. L. Henderson, D. F. Reid, and S. Lepkovsky, *J. Nutrition*, **30,** 175–181 (1945).
[189] H. J. Deuel, Jr., E. Movitt, L. F. Hallman, and F. Mattson, *J. Nutrition*, **27,** 107–121 (1944).

70.6% of the mineralized skimmed milk powder was mixed with 29.4% of the fat containing the fat-soluble vitamin supplement. No differences were observed in the rate of growth of rats at any time over a twelve-week period, irrespective of whether the fat supplied in the diet was a butter, a margarine, or corn, cottonseed, olive, peanut, or soybean oil. The growth, as determined by increase in body weight, was also matched by the bone growth. The graphs illustrating some of these experiments are given in Figures 198 and 199.



Fig. 198. Total gain in weight of male and female rats on diets containing different fats, over a 12-week period.[189]

A similar efficiency in the utilization of the food was observed with the different fats. Moreover, an analysis of the tissues of the rats raised on diets containing the different fats indicated that a similar distribution of protein, fat, carbohydrate, and ash was obtained.[190] This gives added confirmation that growth was equal with the different diets.

In the tests of the Wisconsin investigators, lower growth rates were usually associated with a decreased food intake. Such variations were not noted in the experiments of Deuel and associates. This may have partly been due to the inclusion of diacetyl or butter flavor in the diets in the latter experiments; it was demonstrated that rats prefer a diet of bland fat flavored with diacetyl to one which is unflavored.[191] This explanation

[190] H. J. Deuel, Jr., L. F. Hallman, E. Movitt, F. Mattson, and E. Wu, *J. Nutrition,* **27,** 335–338 (1944).
[191] H. J. Deuel, Jr., and E. Movitt, *J. Nutrition,* **27,** 339–346 (1944).

was later partly discounted by Boutwell *et al.*,[192] since they failed to bring about a sufficient increase in the food consumption by the inclusion of diacetyl in the diet to make growth on the corn oil diet match that obtained on the butter diet; however, some improvement in food consumption and in growth was noted in the experiments of Boutwell *et al.*[192] in which diacetyl was added to corn oil.

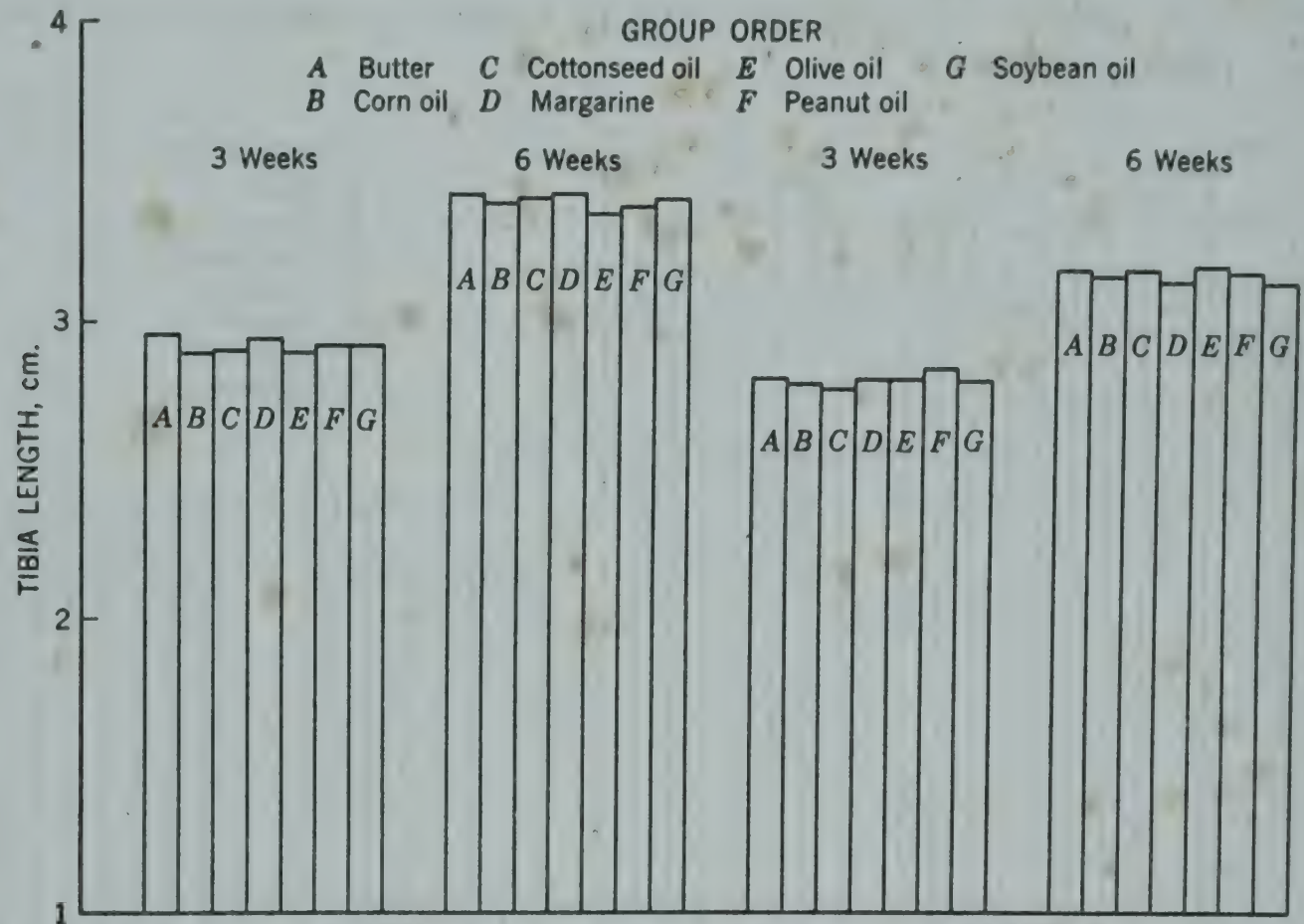


Fig. 199. Tibia length (as an indication of bone growth) of male and female rats after three and six weeks on diets containing different fats.[189]

The criticism which has been raised by Boutwell *et al.* against the experiments of Deuel and associates—because the latter investigators had used unextracted skimmed milk powder—has recently been answered.[193] It was pointed out (by Deuel and co-workers) that no fat extraction of the liquid skimmed milk was employed in the original experiments of the Wisconsin investigators; these experiments showed the greatest discrepancies in growth noted between rats receiving diets containing different added fats. Also, it was found that the method of extraction employed in the later tests of the Wisconsin scientists (four extractions of eight hours each with diethyl ether, during which time there was constant agitation) was effective in removing only a small portion of the 1% of fat in dried skimmed milk powder. Finally, it was found that no appreciable variations in growth resulted in male or female rats fed diets of such extracted

[192] R. K. Boutwell, R. P. Geyer, C. A. Elvehjem, and E. B. Hart, *Proc. Soc. Exptl. Biol. Med.*, **55**, 153–155 (1944).

[193] H. J. Deuel, Jr., C. Hendrick, E. Movitt, M. E. Crockett, I. M. Smyth, and R. J. Winzler, *J. Nutrition*, **31**, 747–753 (1946).

skimmed milk powder irrespective of whether the fat was a butter, a margarine, or corn, cottonseed, peanut, or soybean oil. It would also appear that the amount of any nutritionally important fat present in the skimmed milk powder could only be extremely minute, since most of the long-chain saturated fraction (which is supposed to be the active one in butterfat) is composed of such inactive acids as palmitic and stearic acids.

Oleomargarine was found by Euler, Euler, and Saberg [194] to cause better growth in rats than butter. On diets containing carbohydrates other than lactose, the growth on several margarines and on corn oil was as good as on butter, according to later work of the Wisconsin group.[195]

Boer [196] claimed that butterfat has a superior nutritive value since better growth took place with this fat than with olive oil. This difference was not observed in the tests of the author and his associates to which reference has already been made [189, 190]; however, in later experiments in which olive oil of decidedly inferior quality was used (as determined by free fatty acid content), the growth was considerably inferior to that obtained on diets containing the other vegetable fats or butter.[197] It is possible that the poor growth obtained by Boer with olive oil may have been the result of using an oil of poor quality. Lower growth rates may occur when rancid fats are included in the diet not only because they reduce the appetite for the experimental diet, but also because they may actually destroy some of the dietary essentials.[198]

Altogether, there seems to be considerable evidence that all fats (both animal and vegetable) are equally effective in bringing about growth when such fats are fed as a portion of a diet which compares in composition with whole milk powder. However, Boutwell *et al.*[199] have recently reported that butterfat gives growth superior to that of corn oil when lactose is the carbohydrate and this disaccharide comprises 48% rather than 32% of the diet. This difference was especially evident when the vitamin B intake was restricted. However, no such differences were noted between corn oil and butter when glucose or a galactose–glucose mixture was employed.

One is especially impressed by the inadequacy of lactose as a dietary carbohydrate even when butterfat was used. This deficiency in lactose is further emphasized by Ershoff and Deuel,[200] who found that when this

[194] B. von Euler, H. von Euler, and I. Saberg, *Ernährung,* **7,** 65–74 (1942).
[195] R. K. Boutwell, R. P. Geyer, C. A. Elvehjem, and E. B. Hart, *J. Nutrition,* **26,** 601–609 (1943).
[196] J. Boer, *Acta Brevia Neerland. Physiol. Pharmacol. Microbiol.,* **11,** 180–182 (1941).
[197] H. J. Deuel, Jr., *unpublished observations.*
[198] D. F. Clausen, R. H. Barnes, and G. O. Burr, *Proc. Soc. Exptl. Biol. Med.,* **53,** 176–178 (1943).
[199] R. K. Boutwell, R. P. Geyer, C. A. Elvehjem, and E. B. Hart, *Arch. Biochem.,* **7,** 143–157 (1945).
[200] B. H. Ershoff and H. J. Deuel, Jr., *J. Nutrition,* **28,** 225–234 (1944).

disaccharide was fed at a level of 75%, death of the rats resulted, while the other sugars were well tolerated under similar conditions. One interesting finding which may explain some discrepancies in results in the literature was that a strain difference in the toxicity of lactose was demonstrated by the latter investigators.

2. Results on Prematurely Weaned Rats

In postulating the theory that certain fatty acids are present in butter which are required by very young animals, it was stated by Boutwell *et al.*[201] that the need for butter is accentuated in the very young animals and practically disappears if the animals are kept on a stock diet until 30 days of age. Such results have failed to be confirmed in other laboratories. Zialciti and Mitchell [202] were able to raise rats—which were weaned at seven days—on artificial mixtures containing butterfat or corn oil without observing any superiority of one fat over the other. When rats were weaned at 14 days instead of the usual 21-day period, it was found in the laboratory of the author that diets of corn, cottonseed, peanut, or soybean oils, or a margarine diet afforded equal growth to a similar one containing butterfat.[203]

3. Comparative Effectiveness of Fats in a Low-Caloric Diet

If a specific fat is required during growth, the need for it may be augmented during a period of restricted caloric intake. Under such conditions, it has been found that diets containing corn, cottonseed, peanut, or soybean oils, a commercial hydrogenated fat, a margarine or a butter were equally well utilized.[204] Moreover, no differences were noted in the increased growth response during a period of *ad lib.* feeding following the 12-week period of restricted caloric intake.

4. Comparative Effectiveness of Fats under Conditions of Accelerated Growth

Another criterion of the adequacy of a foodstuff would seem to be its ability to support a growth rate greater than normal. In experiments where such augmented growth was produced by the parenteral injection of pituitary growth hormone, it was found that the diets containing the various vegetable fats (corn, cottonseed, peanut, or soybean oil, or a margarine) supported such growth as effectively as did butterfat.[204] However, had any necessary component been absent in any of the various fat

[201] R. K. Boutwell, R. P. Geyer, C. A. Elvehjem, and E. B. Hart, *J. Dairy Sci.*, **26,** 429–437 (1943).
[202] L. P. Zialciti, Jr., and H. H. Mitchell, *Science*, **100,** 60–62 (1944).
[203] H. J. Deuel, Jr., and E. Movitt, *J. Nutrition*, **29,** 237–244 (1945).
[204] H. J. Deuel, Jr., C. Hendrick, and M. E. Crockett, *J. Nutrition* **31,** 737–746 (1946).

diets, then such lowered nutritive value would have accentuated the difference in growth rate. Not only has it been shown that increased growth does not occur on a diet in which vitamin A is absent when growth hormone is administered, but also that the period of survival under such conditions is definitely shortened.[205] The comparative results of the tests on accelerated growth with various fats are illustrated in Figure 200.

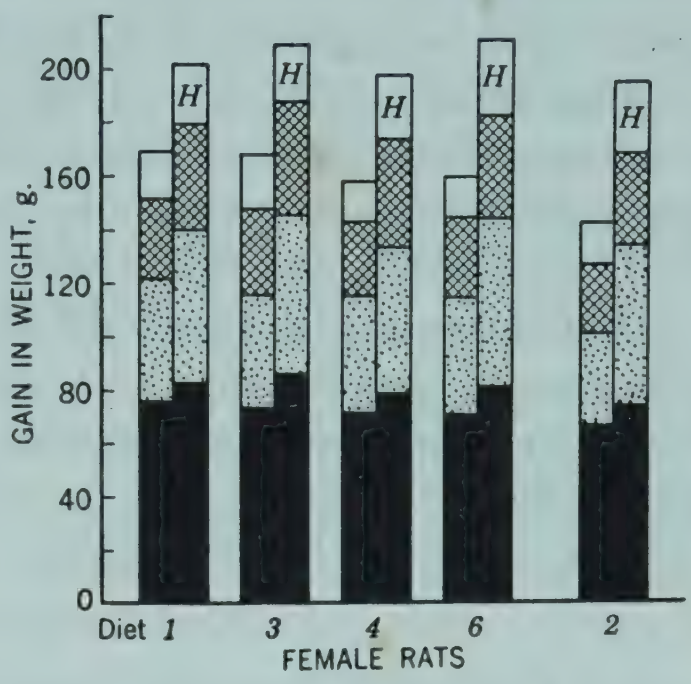


Fig. 200. The average gain in weight of female rats after three weeks (solid black), after six weeks (stippled), after nine weeks (cross hatched), and after 12 weeks (to top of blank space) on diets containing the following (oil or fat): *1*, a butter; *3*, cottonseed oil; *4*, margarine; *6*, soybean oil; and *2*, corn oil. (The experiments on Diet *2* were not all carried out simultaneously with the others.) The columns marked *H* at the top are for the rats injected with growth hormone throughout, and the other column is for the placebo-injected controls.[204]

5. Comparative Effectiveness of Different Fats on Growth of Calves

Gullickson, Fountaine, and Fitch [206] have found that new-born calves grow best on whole milk. When the diet consisted of skimmed milk, homogenized with lard, tallow, coconut, peanut, corn, cottonseed, or soybean oil, growth was decidedly inferior to that on the whole milk. With the last three fats, some of the animals failed to survive. It is difficult to understand these experiments in light of the extensive investigations on rats. It is possible that the calf, because of the peculiar anatomy of the gastro-intestinal system which it has in common with other herbivora, may have different dietary requirements from the rat. Much more evidence should be available on this point. It should be recalled that the gastro-intestinal tract in man resembles that of the omnivorous rat rather than that of herbivorous animals.

6. Ability of Various Fats to Support Pregnancy and Lactation

The dietary requirements for pregnancy and for lactation are progressively more exacting than those for growth. Vinson and Cerecedo [207] have found that a purified diet containing 10% lard and 20% protein (casein) will support growth but not reproduction in the rat. When the

[205] B. H. Ershoff and H. J. Deuel, Jr., *Endocrinology,* **36,** 280–282 (1945).
[206] T. W. Gullickson, F. C. Fountaine, and J. B. Fitch, *J. Dairy Sci.,* **25,** 117–129 (1942).
[207] L. J. Vinson and L. R. Cerecedo, *Arch. Biochem.,* **3,** 389–397 (1944).

protein was increased to 30%, the diet became adequate also for lactation. Sure [208, 209] reached similar conclusions earlier.

It has long been known that fat-free and low-fat diets are especially unsatisfactory for lactation.[2, 210] On otherwise *inadequate* diets, Sure,[211] found that satisfactory lactation was not promoted by butterfat, lard, hydrogenated cottonseed oil, olive oil, or wheat germ oil. However on *adequate* diets, Maynard and Rasmussen [212] were able to demonstrate an improvement in lactation in rats when corn or coconut oil was added to a fat-free diet, although it was later shown by Loosli and co-workers [213] that hydrogenated coconut oil was ineffective. Although Quackenbush, Kummerow, and Steenbock [214] have found that linoleic acid is a requirement for satisfactory milk production, Loosli *et al.*[213] were unable to improve the lactation of rats on a fat-free diet by the administration of 125 mg. of methyl linoleate daily.

TABLE 201

Comparative Nutritive Value of Fats as Determined by Ability to Promote Successful Pregnancy and Lactation[a]

Skimmed milk powder diet mixed with following fat	Pregnancy tests			Lactation tests	
	Animals bred, number	Litters cast, number	Average 3-day weight, g.	Rats died, number	Average 21-day weight, g.[b]
Butterfat	29	29	9.07	23	33.4 (84)
Corn oil	31	28	9.06	1	32.9 (112)
Cottonseed oil	31	30	9.15	2	34.2 (98)
Margarine fat	35	33	7.57	8	34.8 (112)
Olive oil	23	18	7.88	1	35.2 (70)
Peanut oil	32	31	8.03	4	33.6 (84)
Soybean oil	28	26	7.60	1	32.4 (98)

[a] H. J. Deuel, Jr., E. Movitt, and L. F. Hallman, *J. Nutrition*, **27**, 509–513 (1944).
[b] Average weight of seven rat litters only. Figures in parentheses are the number of rats.

From a qualitative standpoint, it was found by Deuel *et al.*[215] that corn, cottonseed, peanut, and soybean oils, and a vegetable oil margarine are as satisfactory dietary fats in insuring successful pregnancy and lactation as is butter. The results on olive oil were somewhat less satisfactory, but it is believed that this is partly to be ascribed to the poor quality of

[208] B. Sure, *J. Biol. Chem.*, **58**, 693–709 (1923–1924).
[209] B. Sure, *J. Biol. Chem.*, **62**, 371–396 (1924).
[210] E. B. Meigs, *Physiol. Revs.*, **2**, 204–237 (1922).
[211] B. Sure, *J. Nutrition*, **22**, 499–514 (1941).
[212] L. A. Maynard and E. Rasmussen, *J. Nutrition*, **23**, 385–398 (1942).
[213] J. K. Loosli, J. F. Lingenfelter, J. W. Thomas, and L. A. Maynard, *J. Nutrition*, **28**, 81–88 (1944).
[214] F. W. Quackenbush, F. A. Kummerow, and H. Steenbock, *J. Nutrition*, **24**, 213–224 (1942).
[215] H. J. Deuel, Jr., E. Movitt, and L. F. Hallman, *J. Nutrition*, **27**, 509–513 (1944).

the olive oil available. When female rats, which had been raised on skimmed milk powder and one of the fats, were bred with males raised on the same diet, the fertility of the females exceeded 90% on all diets except that made up of olive oil. Moreover, the ability of such diets to provide satisfactory lactation, as judged by the number of young alive at 21 days and their weight at that age, was as promising for the vegetable oils as for butter. These data are summarized in Table 201.

G. Ability of Vegetable Fats to Support Growth and Reproduction over a Number of Generations

The ultimate test for any food would seem to be its ability to preserve health and to promote well being over a number of generations. Foods that at first seem to be satisfactory for growth, pregnancy, and lactation might, after several generations, fail to exhibit such potency if any inadequacy is present, since the deficiencies might be cumulative.

Although there are many reports of instances where persons have partaken of an exclusively vegetable diet throughout life, the components of the diets can not be constantly uniform and the observations are generally without scientific precision; it is therefore impossible to draw deductions about the adequacy of any single food from such records. Moreover, it is obviously impractical to confine individuals to any fixed regimen over a period of years, let alone over a number of generations. A much more satisfactory method of approaching the solution of this problem is by the use of rats with which a uniform simple diet can be continuously employed and three generations a year can be raised.

Sherman and his collaborators[216] have carried out studies of this nature on diets containing butterfat. On their diet B, which consists of 66% whole ground wheat, 33% whole milk powder, and 1% sodium chloride, they have maintained a colony of rats over a span of 50 generations. The diets were supplemented weekly with a small amount of lean meat and lettuce. Similar tests have recently been reported by Deuel *et al.*,[217] but in this case the butterfat was replaced by a vitamin A-fortified margarine fat. Successful growth and reproduction was maintained for 10 generations in which the lineage was through the first litter, and for eight generations in which the lineage was through the second litters, at the last report.[217] At the present time (October, 1947), the experiments on the first litter rats have continued successfully to the nineteenth generation. The rats have maintained an excellent growth rate which has considerably exceeded that of rats on the stock diet. It is considered that this experiment answers affirmatively the question raised by Boutwell *et al.*[201] as to the adequacy of a vegetable fat to suffice for continued growth and

[216] H. C. Sherman and H. L. Campbell, *J. Nutrition*, **2**, 415–417 (1930).
[217] H. J. Deuel, Jr., L. F. Hallman, and E. Movitt, *J. Nutrition*, **29**, 309–316 (1945).

reproduction over a number of generations. Thus, on a diet otherwise nutritionally adequate, it would seem that a vegetable fat, such as that contained in margarine, can serve the needs for growth and reproduction over a number of generations as well as can butter.

H. Role of Fats in Preventing Galactosuria Occurring on an Exclusive Skimmed Milk Diet

Another pertinent feature of fat metabolism is the ability of a specific fat to cause the utilization of galactose on diets of skimmed milk. It has long been recognized that the metabolism of galactose differs considerably from that of glucose.[218] Schantz, Elvehjem, and Hart[219] have reported the very interesting observation that an excretion of galactose occurs in the urine of weanling rats on a mineralized skimmed milk diet. As much as 35% of the galactose which could have arisen from the ingested lactose of the milk was found in the urine. Fats, in general, could largely abolish this galactosuria. When the diet consisted of mineralized skimmed milk to which 3 to 4% of butterfat, lard, corn oil, linseed oil, or even palmitic or oleic acids were added, the sugar excretion stopped. These results were obtained not only with liquid skimmed milk, but also with powdered skimmed milk. In earlier tests where fat made up 11% of the ration, Mitchell, Cook, and Merriam[220] observed a galactosuria of varying degrees in rats receiving a high-lactose or galactose diet. On the other hand, Schantz and Krewson[221] found that even-chain fatty acids containing 12 or more carbon atoms were effective, while those containing less than 12 carbons or containing odd chains were useless in protecting against such a galactosuria. Glucose was only slightly active in this regard. The recent report of Zialciti and Mitchell[222] gives the only evidence of qualitative differences between the fats in promoting the utilization of the galactose. From the results of Schantz and Krewson,[221] it might be expected that butterfat would be somewhat less active than the other animal and vegetable fats which did not contain the inactive short-chain acids present in butter. In support of this, Zialciti and Mitchell[222] have reported a series of clear-cut experiments which demonstrate that corn oil but not butterfat is able to reduce the galactose excretion of young rats on a diet containing 48% lactose. Nieft and Deuel[222a] found no difference in effects of butterfat, corn oil, and cottonseed oil when fed at a 20%

[218] H. J. Deuel, Jr., *Physiol. Revs.*, **16,** 173–215 (1936).
[219] E. J. Schantz, C. A. Elvehjem, and E. B. Hart, *J. Biol. Chem.*, **122,** 381–390 (1938).
[220] H. S. Mitchell, G. M. Cook, and O. A. Merriam, *J. Nutrition*, **13** (supplement), 18 (1937).
[221] E. J. Schantz and C. F. Krewson, *Proc. Soc. Exptl. Biol. Med.*, **42,** 577–579 (1939).
[222] L. P. Zialciti, Jr., and H. H. Mitchell, *J. Nutrition*, **30,** 147–150 (1945).
[222a] M. L. Nieft and H. J. Deuel, Jr., *J. Biol. Chem.*, **167,** 521–525 (1947).

level on the resulting galactosuria, but, at the 10% level, cottonseed oil feeding resulted in a significantly lower urinary galactose excretion than either butterfat or corn oil. These authors believe that the chief effect of the fat is related to the slowing of the rate of absorption of galactose from the intestine; however, their evidence does not entirely preclude a metabolic effect of fat on galactose utilization. It is of importance that further studies with other fats be carried out to understand the reason for the lactose-fat interrelation. While at present no conclusions on the comparative value of fats can be postulated from the present data, it would appear questionable that butterfat is the fat *par excellence* for metabolism with lactose.

IV. Optimum Level of Fat in the Diet

A. Dietary Studies as a Method for Evaluation

An estimate of the optimum level of fat in the diet for the United States, based on the average consumption of this foodstuff, would be 125 g. daily or approximately 33% of the total calories.[223] On the other hand, the daily fat intake of the Japanese, prior to 1930, was only 29 g.—and that of the British people, 106 g. The latter figure had increased to a value comparable to that of the American dietary by 1934, namely, 124 g. per day. Contrasted with these values are the extremes brought on by the recent war, varying from a level of less than 3% of the total calories reported for the soldiers in South China [224] to the high value of 40% for the American soldier (or a daily consumption of 193 g.[225] Although the normal height–weight relationship of the Chinese soldier has thus far been maintained on the low-fat ration, periods—even of several years—are obviously too short for any critical evaluation on the human of the effect of a defective diet. The high level of fat in the diet of the American soldier has possibly been one of the contributing factors to the excellent nutrition maintained in the armed forces of this country during World War II. The Committee on Foods of the National Research Council recommended [226] that in the rationing of foodstuffs, during the period of critical fat shortage brought on by World War II, the average minimum annual fat allotment be set at 68 pounds per person, which could be met by 40 pounds of "visible" fat and 28 pounds of "invisible" fat (*i.e.*, fat in the foods). This quantity would give a daily quota of only about 84.6 g. of fat.

The level of fat intake is obviously not only a question of food habits and national tastes, but also one of availability. One can only say that the analysis of dietaries indicates that a fat intake at a level as low as 3%

[223] K. Brandt, *Ann. Am. Acad. Polit. Soc. Sci.*, **225,** 210–215 (1943).
[224] T. Shen, *Science,* **98,** 302–303 (1943).
[225] P. E. Howe, *Ann. Am. Acad. Polit. Soc. Sci.*, **225,** 72–79 (1943).
[226] *National Research Council Reprint and Circular Series,* **No. 118** (1943).

of the total calories can be maintained over several years; one can also conclude that a diet containing 40% of the calories in fat can not only be well tolerated but also can result in an excellent nutritional picture.

B. Growth Experiments on Rats as a Method for Evaluation

Although Burr[6] has been able to produce growth in rats on diets practically devoid of fats, provided the fat-soluble vitamins and the essential fatty acids were supplied, the growth response was not as great as on diets which contained a greater proportion of fat.

Similar differences have been noted by other workers in the field. For example, Ellis *et al.*[120] obtained about twice the growth in rats when fat was supplied at a 12% level as contrasted with a diet containing 3%. The gains in weight on cottonseed oil diets at the 3 and 12% levels were 71 g. (66 days) and 121 g. (51 days), respectively, while the corresponding values for Crisco were 67 g. (56 days) and 142 g. (51 days).

Hoagland and Snider[227] found in most cases a progressively greater growth when lard was fed at levels of 5, 30, and 55% of the diet, which constituted 12, 53, and 78%, respectively, of the total calories. At the level of 5%, cottonseed oil and peanut oil induced the largest gain in weight. When the fats comprised 30% of the diets, the largest gains were scored by the animals receiving refined lard, leaf lard, and peanut oil; whereas there was no additional growth in the cottonseed oil group over animals which received this oil at the 5% level. The vegetable oils were not fed at the highest level, so no further comparisons are possible. It should be borne in mind that the most satisfactory rat tests on diets consisting of high levels of fat are made with fats which have a melting point somewhat above room temperature. Otherwise, the diets are difficult for the animals to eat and are much more readily susceptible to rancidity.

The level of fat in the diet previous to fasting has recently been shown to be related to the period of survival during a subsequent fast. Those rats which had previously been forcibly fed on a high-fat diet were found to survive for a longer period than those which had received an equicaloric high-carbohydrate diet during the preliminary period.[228] A marked difference in susceptibility to injected insulin was also observed.[229] The rats which had been accustomed to the high-fat regimen were much less sensitive to the hormone, which was ascribed to the more prolonged retention of liver glycogen. Roberts, Reinecke, and Samuels,[230] in an extension of this work, were led to believe that animals fed on a diet in which 85% of the calories come from fat develop a sparing action for carbohydrate.

[227] R. Hoagland and G. G. Snider, *U.S. Dept. Agr. Tech. Bull.*, **725** (1940).
[228] S. Roberts and L. T. Samuels, *Bull. Minnesota Med. Foundation*, Feb., 1944.
[229] S. Roberts and L. T. Samuels, *Proc. Soc. Exptl. Biol. Med.*, **53**, 207–208 (1943).
[230] S. Roberts, L. T. Samuels, and R. M. Reinecke, *Am. J. Physiol.*, **140**, 639–645 (1944).

When the livers were removed from such rats, they lived longer and were free of hypoglycemic symptoms for a greater interval than were rats which had previously been given a diet of high-carbohydrate content.

One must conclude that fats improve nutrition but the optimum level in the diet is still uncertain. It would seem that not only growth, but the ability to support pregnancy and lactation, the effect on the capacity for work, longevity, and such additional factors should be considered. Finally, it is altogether possible that qualitative differences may be found in the optimum fat level with the different fats.

V. General Considerations

There is no single animal or vegetable fat which is superior in all respects. With few exceptions, practically all fats are equal as sources of calories since they are for the most part digested to an extent of 95% or better. The only fats which are less efficient as sources of energy are those which are less completely digested. In this group are those fats with a relatively high melting point, such as mutton tallow, oleostearine, and some very completely hydrogenated vegetable fats.

A limited number of animal fats, such as butter, egg yolk, and liver fat, may be good sources of vitamin A, although other animal fats including lard, beef tallow, and mutton tallow do not contain any appreciable quantity of this vitamin. Palm oil and the fatty components of green leaved plants are usually excellent sources of provitamin A.

Vitamin D is largely absent both from animal and vegetable fats, although appreciable amounts may be present in milk after feeding the cow large amounts of irradiated ergosterol. The most concentrated sources are the fish liver oils. However, vitamin D may be produced artificially by irradiation of certain animal and vegetable oils.

Vitamin E or α-tocopherol is widely distributed in seed oils where it is concentrated in the germ. The best natural sources are wheat germ, soybean, and cottonseed oils, as well as a large number of other vegetable oils. The amounts in animal fat are quite insignificant. Thus, the vegetable oils are the main sources of this essential vitamin and for this reason they have the added advantage of a greater stability due to the antioxidant activity of the tocopherols.

The vegetable oils as a rule excel the animal fats on the basis of the proportion of the so-called essential fatty acids. Many of the vegetable oils, such as cottonseed, grapeseed, hempseed, linseed, poppy seed, soybean, sunflower seed, walnut, and watermelon seed, have a total essential fatty acid content varying between 50 and 75%. The unsaturated acids (other than oleic, which is not included in the category of essential fatty acids) are usually quite low or absent in animal fats, except in a few cases in which the animals from which the fat was derived have been on

diets rich in the unsaturated acids. Even in these cases, the proportion of the essential acids is very much lower than in many vegetable fats. Although many animal fats are unique in possessing a small amount of arachidonic acid which the vegetable fats do not contain, there is no evidence of any specific function of arachidonic acid which cannot as effectively be met by linoleic acid.

As might be expected from their composition, the vegetable and animal fats compare favorably when tested in nutrition experiments on animals. The vegetable fats with a high content of essential acids are most effective in the treatment of the fat-deficiency disease. There is no evidence that linoleic acid, present in high concentration in the seed oils, will not accomplish the same results as the arachidonic acid, which appears in small amounts in some animal fats. When the diet supplies adequate quantities of vitamins A and D, it would appear that animal and vegetable fats are equally efficient in promoting growth, both under normal conditions and where an abnormally rapid growth has been produced by a growth hormone. When there is a restricted food intake, a similar situation results. Animal and vegetable fats also serve equally well in pregnancy and lactation. This is of special significance with respect to their evaluation, since the effect on lactation is one of the most critical tests that can be applied in determining the nutritive quality of a foodstuff.

Although hydrogenation largely effects a conversion of linoleic acid to oleic acid, analyses indicate that all hydrogenated fats, melting in the usual range of the margarines and shortenings (approximately 35–40° C.), may still contain 10% or more of acids more unsaturated than oleic. The presence of the iso-oleic acids which usually result from hydrogenation does not cause a lower utilization of the fat. Elaidic acid, one of the isomers, is well utilized in the rat and presumably in man. Products of the blended type have a much larger proportion of linoleic glycerides and a minimum amount of iso-oleic acids, since mixtures largely melting at body temperature will consist of more than two-thirds of the untreated oil.

The important nutritive qualities which are attributable to the vegetable oils are largely retained and in some cases augmented by partial hydrogenation of the oils. The digestibility of hydrogenated vegetable fats melting below 50° C. is practically complete in man, and is as satisfactory as that of other animal and vegetable fats. This is also true of the so-called "blended hydrogenated fats," made by mixing a portion of completely hydrogenated fat of high melting point with untreated oil, provided that the mixture melts below 50° C. Growth, pregnancy, and lactation proceed normally when such hydrogenated fats make up practically the entire fat content of the diet. Experiments with rats in which practically the entire fat of the diet was supplied by margarine have continued successfully over 19 generations.

There is no reason to suppose that the mono- or diglycerides used in the so-called "high-ratio" or "superglycerinated" shortenings should be any less effectively absorbed and utilized than the usual triglycerides. It has long been recognized that when fatty acids are fed as such they are readily absorbed and synthesized into triglycerides. The animal organism seems to be able to manufacture as much glycerol as is needed for such purposes.

One difference in metabolism, which would probably be noted especially in the case of the monoglyceride as compared with the triglyceride, is that an appreciable amount of carbohydrate would immediately become available after absorption. This is because the monoglyceride would be converted into the triglyceride after absorption and would then be capable of being further metabolized or stored. Thus, for each three molecules of monoglyceride, two molecules of glycerol would not be used for triglyceride synthesis and would thus be available for conversion to glucose. Glycerol can be converted to glucose to the extent of 100%.[127] It is hoped that some additional experimental evidence on further features of the metabolism of the mono- and diglycerides will become available.

The subject of fat metabolism is still a dynamic rather than a static one. Much research is in progress which will help to answer some of the most perplexing problems. We can look for an early answer on such subjects as comparative rates of absorption, the mechanism of antioxidants, and the optimum fat level in the diet.

CHAPTER XX

NONEDIBLE COTTONSEED OIL PRODUCTS

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I. Introduction

Almost the entire production of cottonseed oil is used for edible products. The proportion of the oil going directly into nonedible products is shown in Table 202 to be little more than one-half of one per cent of the total consumption. The low consumption in the nonedible field may be explained in part by the nature of the fatty acids and also in part by economic factors.

TABLE 202

Nonedible Consumption of Crude and Refined Cottonseed Oil[a]

Measurement	1942[b]	1943	1944
Total consumption of crude oil, 1000 pounds	733,493	1,331,642	1,136,074
Quantity of crude and refined oil used in nonedible products, 1000 pounds	4,496	7,286	5,813
Percentage of oil used in nonedible products based on total oil consumption	0.61	0.55	0.51

[a] Compiled from U.S. Bureau of the Census, *Animal and Vegetable Fats and Oils, Calendar Years 1940–44.*
[b] Last six months only.

Cottonseed oil belongs to the oleic-linoleic acid group of fats. The relative proportions of fatty acids in the oil are approximately: 25% saturated fatty acids, largely palmitic; 30% monoethenoid acids, largely oleic; and 45% diethenoid acids, principally linoleic. Because of this fatty acid composition, cottonseed oil is especially desirable for edible purposes. It can be made into a salad or cooking oil by winterizing, or it can be hydrogenated to the desired plasticity for shortening or margarine. There is little danger of flavor reversion since the oil contains no fatty acids more unsaturated than linoleic. Hence the oil has consistently commanded a leading position in the edible field.

On the negative side, cottonseed oil is not sufficiently unsaturated to be of value as a drying oil in the paint and protective coating industry. Furthermore, it is not as satisfactory a material for soap manufacture as lower priced fats, such as tallow, grease, and coconut oil. Its direct use in soap has been minor and incidental. Table 203 shows a comparison of

TABLE 203

Selected Comparative Wholesale Prices for Cottonseed Oil and Other Fats[a]

Year	Average value, cents per pound		
	Cottonseed oil[b]	Coconut oil, crude[c]	Tallow, packers' prime[d]
1934	6.5	4.6	4.2
1935	10.4	7.4	7.0
1936	9.8	8.0	6.6
1937	9.2	9.0	8.2
1938	7.9	6.1	5.6
1939	6.6	6.1	5.4
1940	6.2	5.6	4.5
1941	10.5	8.4	7.6
1942	13.9	10.9	9.2
1943	14.0	11.0	8.6
1944	14.2	11.0	8.6

[a] From U.S. Department of Commerce, *Annual Review-1944, Fats and Oils.*
[b] Prime Summer Yellow (P.S.Y.), tank cars, New York.
[c] Manila, crude, tanks, f.o.b. Pacific Coast; includes excise tax of three cents.
[d] Inedible packers' prime, Chicago.

TABLE 204

Cottonseed Oil Refining Losses in the United States[a]

Measurement	1942[b]	1943	1944
Crude oil used in refining, 1000 pounds	732,161	1,329,801	1,135,466
Production of refined oil, 1000 pounds	684,974	1,241,156	1,061,927
Loss	47,187	88,645	73,539
Percentage loss based on crude oil used	6.44	6.68	6.47

[a] Compiled from U.S. Bureau of the Census, *Animal and Vegetable Fats and Oils, Calendar Years 1940–44.*
[b] Last six months only.

wholesale prices for cottonseed oil, packers' prime tallow, and crude coconut oil for the period 1934 to 1944.

The relatively high price of cottonseed oil is probably a factor against its general consumption in other industries where its application might otherwise be acceptable.

While only a few million pounds yearly of nonedible products are derived directly from cottonseed oil itself, a very considerable source of nonedible products consists of the foots or soapstock, which are a by-product of edible oil processing. Table 204 shows that the annual refining loss from cottonseed oil processing is upwards of 70,000,000 pounds of anhydrous fatty material. The present chapter will, therefore, be devoted largely to a discussion of the processing and the utilization of cottonseed oil foots.

Soapstock is derived from the alkali neutralization of the fatty acids in crude oil. It consists mainly of soap, entrained neutral oil, nonfatty organic substances, and moisture. The fatty acid constituents in foots are little, if any, different in proportion to each other than the corresponding acids found in the original crude oil.

Foots, in contrast to the oil from which they are derived, are low in cost on a fatty acid basis. They are of value to industry because of their recoverable fatty acid content.

A typical analysis [1] of soapstock from batch kettle refining is shown in the accompanying table.

Constituent	Per cent
Moisture	45.6
Neutral oil	18.7
Fatty acids from soap	24.0
Ash as sodium oxide	3.3
Nonfatty substances	8.0

Foots from batch refining operations usually contain between 40 and 50% total fatty acids. Foots from continuous, centrifugal, caustic refining contain approximately 35 to 45% total fatty acids, the ratio of neutral oil to fatty acids from soap being approximately two to five. In the continuous process employing soda ash as the neutralizing agent, soapstock contains about 30 to 40% total fatty acids, with an approximate ratio of one part neutral oil to four parts fatty acids from soap. The latter product may fall below 35% total fatty acids, depending upon the degree of rehydration employed in the process.

With the increased usage of continuous refining methods in the United States, the quality of foots has deteriorated. The ratio of organic nonfatty substances to total fatty acids in foots has increased considerably. This is primarily due to reduction of the amount of entrained oil in foots and reduced saponification of neutral oil made possible by continuous refining methods.

[1] G. S. Jamieson, *Vegetable Fats and Oils*, Reinhold, New York, 1943, p. 206.

II. Methods of Handling Foots

A. Raw Soapstock

A considerable amount of soapstock is handled in the raw state and is used as such in soap works and fatty acid distillation plants connected with the refinery, or is shipped in tank cars or trucks to outside soap works and distillers. Soapstock is sold on the basis of 50% total fatty acid content.[2] The purchaser has the right to reject a shipment if the total fatty acid content is below 35%.

B. Acidulated Soapstock

In order to reduce freight charges, much of the soapstock is acidulated before shipment. It is usually shipped in tank cars and drums, mainly to distillers, and is sold on the basis of 95% total fatty acid content.[2] The buyer has the right to reject shipment if the fatty acid content falls below 85%.

Acidulated soapstock is prepared by boiling raw soapstock with a slight excess of sulfuric or other mineral acid in wood or lead-lined vats until the soap is thoroughly decomposed. The charge is then settled, and a layer consisting of fatty acids and neutral oil forms on top. This layer is a black, oily liquid, somewhat strong in odor. It is decanted from the aqueous bottom layer and is then ready for storage or shipment.

C. Boiled-Down Soapstock

A small quantity of raw foots are processed into boiled-down soapstock, which is usually sold in slack barrels on the basis of 65% total fatty acid content. There are advantages to be gained by this treatment. Boiled-down soapstock, unlike the raw foots, can be stored indefinitely with little danger of deterioration. Furthermore, the improved quality of boiled-down soapstock makes it a more acceptable product than raw or acidulated foots, especially for the small soap trade.

Boiled-down soapstock is prepared in a manner similar to that used for the production of regular, full-boiled soap. Raw foots are charged to a kettle and boiled on open steam with a slight excess of caustic soda until saponification of the neutral oil is completed. The kettle is "grained" with salt brine to separate the soap curd from the wash. After a short time, the brine wash water which has settled to the bottom of the kettle is run off and discarded.

Several more individual brine washes are given to the kettle in the same manner, for the further removal of impurities from the soap. After the final brine wash is drawn off the kettle, the soap curd is boiled down

[2] National Cottonseed Products Association, *Rules Governing Transactions Between Members,* 1945–1946.

on closed steam coils for several hours, until sufficient water is vaporized to increase the fatty acid content of the soap curd from about 56% initially to 65% in the final product. The boiling-down operation also serves to remove much of the steam-volatile odorous compounds. While still hot, the soapstock is run into slack barrels or other containers for storage and shipment.

Properly cleansed, boiled-down soapstock is fairly firm, yellow to light brown in color, and of a characteristic, not unpleasant, odor. Since it is used mainly in the manufacture of high-alkali soap powders and highly built, yellow laundry bar soap, color and odor are not of critical importance.

To conserve materials, countercurrent washing is sometimes employed to cleanse the soap of impurities. The results are equally as good as those obtained with the individual wash system.

D. Settled Soapstock

Settled soapstock is processed in the same manner as boiled-down soapstock except in one particular. In the final kettle operation, after the last brine wash is drawn off, the soap curd is not boiled down but is given a "fitting" change. The curd is boiled with additional water and is allowed to settle into two layers. The top layer is settled "neat" soap and the bottom layer, "niger."

The neat soap layer, which contains about 60 to 62% fatty acids, is drawn off into slack barrels or other containers for storage and shipment as settled soapstock.

Settled soapstock is of better quality than boiled-down soapstock, since a large proportion of the impurities settle out into the niger during the fitting operation. Both boiled-down and settled soapstock command a higher price based on equivalent fatty acid content than raw or acidulated foots. However, the production of boiled-down and settled soapstock is normally of minor trade importance.

III. Glycerin Recovery

It has not been found economical to recover glycerin from cottonseed foots. The lyes and sweet-waters from saponification of the foots are low in glycerol and contain most of the organic impurities of the foots. These impurities are not effectively removed during glycerin processing operations and eventually find their way into the finished distillate.

Several successive redistillations of the glycerin will eventually produce a distillate meeting the specifications for pure and high-gravity grades. However, the additional cost for redistillation, together with distillation losses, make such an operation uneconomical under most market conditions.

IV. Fatty Acid Distillation

A. Pretreatment of Foots

The primary objective of the distillation of fatty acids derived from foots is the production of light-colored fatty acids. Much of the success of that operation depends on the pretreatment of the foots before distillation.

Foots are purchased by the fatty acid distiller either as raw soapstock or as acidulated soapstock. Raw soapstock is processed as promptly as possible after receipt. It may be acidulated, settled, and dried as previously described.

It is desirable, in any event, to treat the stock to be distilled in such manner as to obtain the highest degree of splitting of the neutral oil. To achieve this end, raw soapstock as received may be treated in low-pressure autoclaves operating at 100 to 150 p.s.i. steam pressure. The soap present in the foots acts as a catalyst to complete the saponification of the neutral oil. After saponification, the mixture is then removed from the autoclave and boiled with sufficient sulfuric acid to decompose the soap. The fatty acids are decanted, washed, and dried, and are then ready for distillation.

While not in general use, the method for obtaining the most complete split of the neutral oil is as follows. Saponification of the raw soapstock is completed in soap kettles with additional caustic soda, and the washing operation is carried out as described in the method for preparing boiled-down soapstock. However, after the last brine wash is run off, the soap curd is decomposed by means of a mineral acid; and the fatty acids are decanted, washed, and dried to prepare them for distillation.

It is claimed [3] that the fatty acid distillation yield from foots prepared by the soap boiling method is 95%, and the distillate is of measurably better quality than that obtained from foots prepared by other methods.

The soap boiling method has much to commend it. Equipment required is simple and relatively inexpensive, consisting mainly of soap kettles. The low temperatures employed are not harmful to unsaturated double bonds in the fatty material. Relatively little extra caustic soda is required to complete the saponification of the small amount of entrained neutral oil in foots derived from modern continuous refining processes.

Acidulated foots are sometimes fed directly to the still with no further treatment other than drying. However, the preferable practice is to saponify the neutral oil in the foots as completely as possible before distillation. The yield of fatty acids on distillation is appreciably increased when this practice is adhered to.

[3] H. D. Hoffman and A. H. Zeigler (to Armour & Co.), U.S. Pat. 2,319,929 (1943).

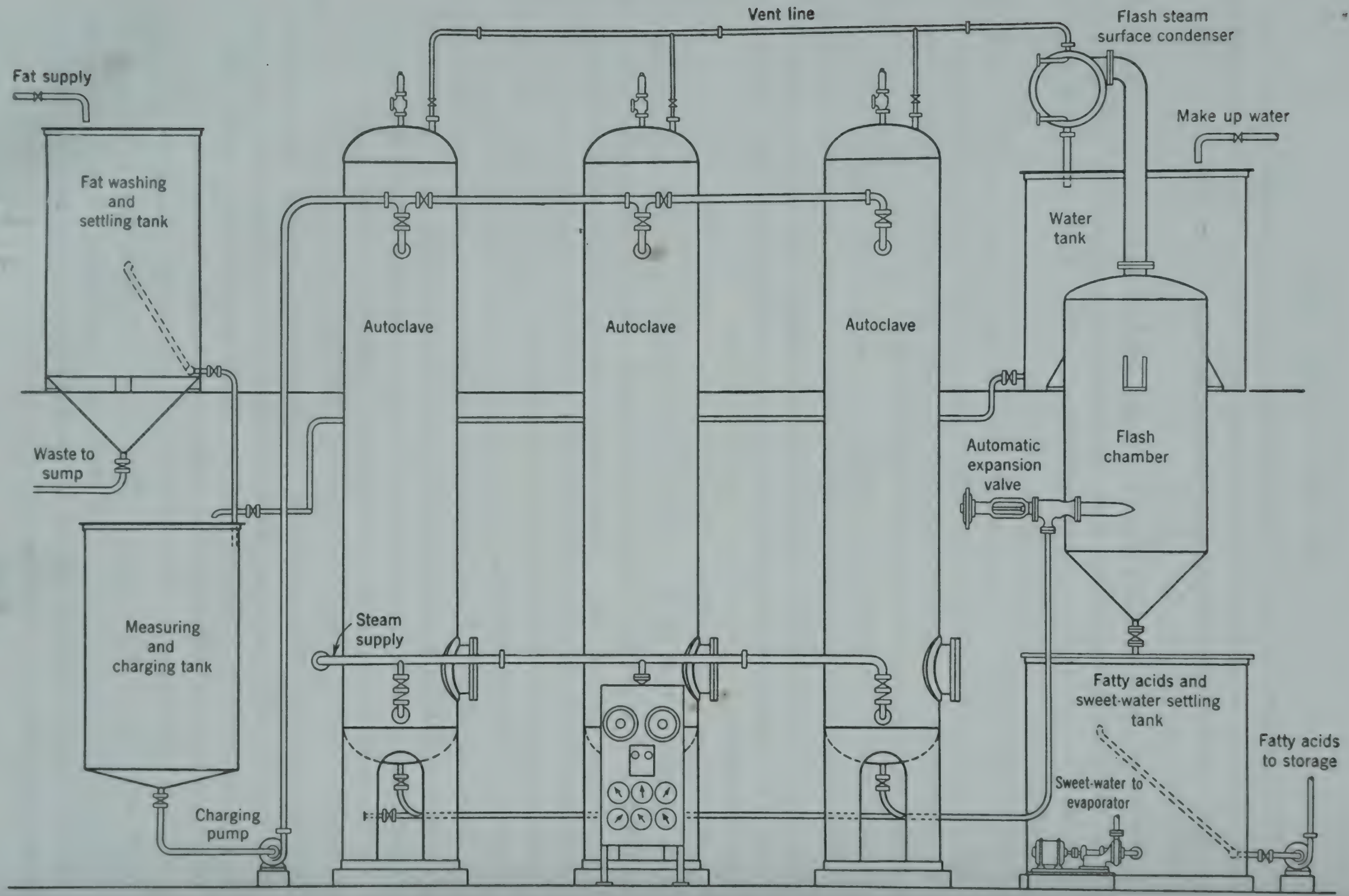


Fig. 201. High-pressure autoclave fat splitting system. (Courtesy *Wurster & Sanger, Inc.*)

If the acidulated foots are fed directly to the still without splitting, it is common procedure to collect the residue, or "still bottoms," and split the neutral oil contained therein for further recovery of distillable fatty acids.

Although the volume of the fatty material to be split is reduced greatly by this practice, the amount of polymerized fatty material in the residue is increased and the yield of fatty acids is thereby decreased.

There are several methods for splitting acidulated foots. One method is to split the foots in low-pressure autoclaves, utilizing a catalyst to complete the saponification. If high-pressure autoclaves operating at 350 to 400 p.s.i. steam pressure are available, no catalyst is required—the water added reacting directly with the neutral oil at the operating temperature. A typical high-pressure autoclave fat splitting system is illustrated in Figure 201.

Continuous methods [4, 5] of fat splitting, which are adaptable to acidulated foots,[6] are in the process of being developed. Operating pressures used in these methods are in the range of 600 to 3,500 p.s.i.

Plants not equipped with any of the pressure systems of splitting utilize the well-known Twitchell process for splitting the acidulated foots.

Further pretreatment of the crude fatty acids prior to distillation has been studied to some extent, primarily to obtain color stability in the distilled product.

A method is described by Sheely [7] for heat treating cottonseed fatty acids before distillation. The fatty acids are processed with hydrogen in the presence of 0.5% of spent nickel bearing hydrogenation catalyst for two hours at 75 p.s.i. and 200° C. (392° F.). A sample of distilled fatty acids from stock treated in this manner is claimed to have had good color stability after being given an accelerated aging test. However, the equipment required for this method of treatment is expensive, since material resistant to fatty acid corrosion must be employed.

B. Distillation Methods

A large proportion of the fatty acids from cottonseed foots are distilled by the older batch method.[8] Batch distillation is conducted under absolute pressures of 12 to 50 mm. of mercury, usually in a direct-fired, cast iron still at a temperature of about 260° C. (500° F.), with the aid of superheated steam. Stock is fed to the still until the distillate becomes highly colored. The feed to the still is then discontinued and the accumulated residue in the still, consisting mainly of neutral oil, polymerized fatty

[4] M. H. Ittner (to Colgate-Palmolive-Peet Co.), U.S. Pat. 2,139,589 (1938).
[5] V. Mills (to Procter & Gamble Co.), U.S. Pat. 2,156,863 (1939).
[6] N. G. Robisch (to Procter & Gamble Co.), U.S. Pat. 2,267,750 (1941).
[7] M. L. Sheely (to Armour & Co.), U.S. Pat. 2,062,837 (1936).
[8] O. H. Wurster, *Chem. & Met. Eng.*, **25**, 651 (1921).

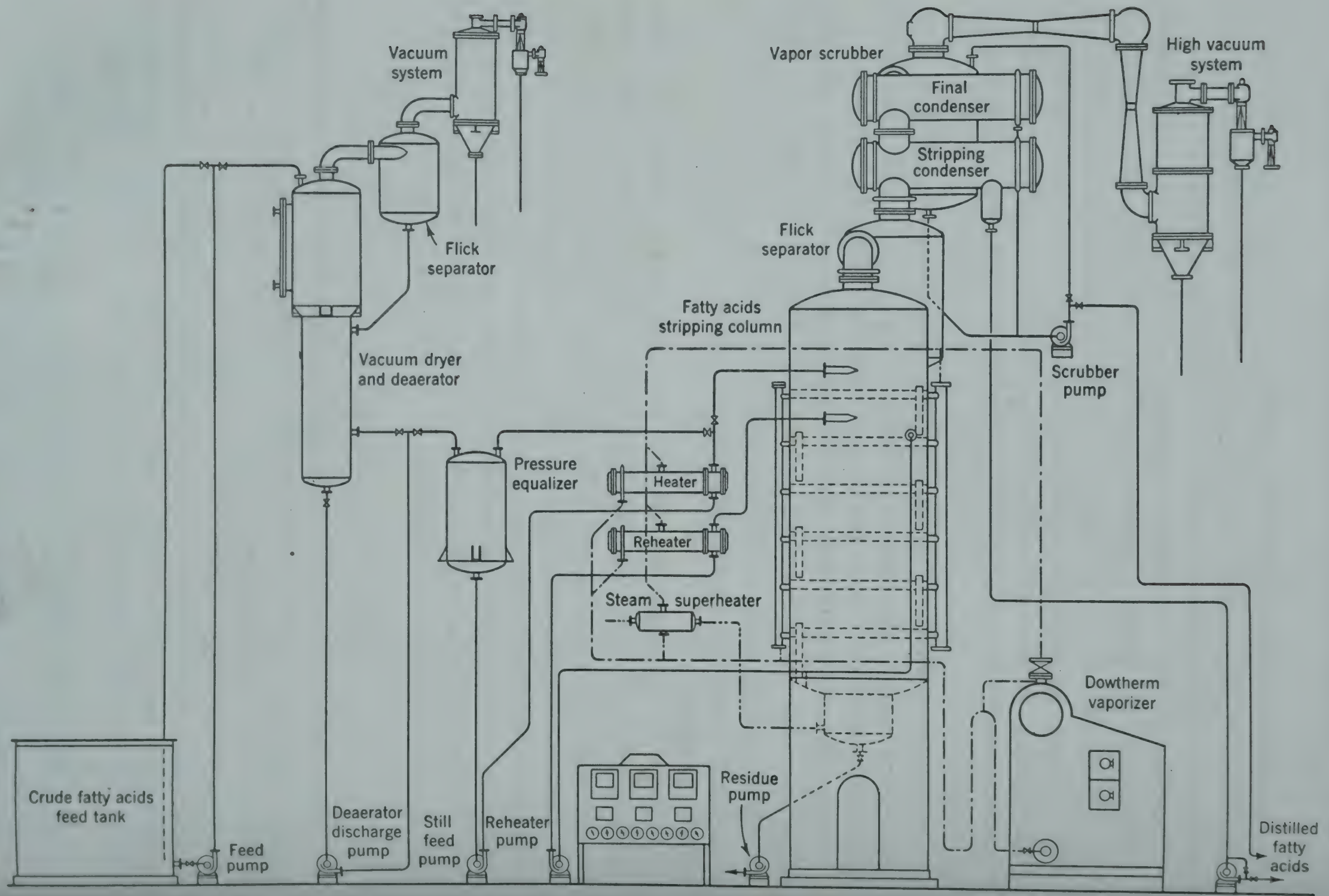


Fig. 202. Continuous fatty acid distillation system. (Courtesy *Wurster & Sanger, Inc.*)

material, and organic impurities, is run down at higher temperatures to pitch. The distillate so obtained is redistilled. The pitch is subsequently removed from the still, cooled, and barreled for sale. Double distillation is necessary to obtain light colored fatty acids. The yield of double-distilled fatty acids from acidulated cottonseed foots is about 85%.

Improved and continuous methods of fatty acid distillation have been made possible by indirect heating, lower absolute pressures through use of multistage steam jet ejectors, and improved materials of construction.

Continuous methods [9-11] employ steam or flash distillation under absolute pressures of 1 to 50 mm. The stock is fed into the still continuously. The residue which accumulates at the bottom of the still is discharged continuously, together with some admixed fatty acids. The mixture of residue and fatty acids is recycled or stored for future batch distillation. When sufficient residue is accumulated, the neutral fat in it may be split further and then stripped of fatty acids in a batch still or run to pitch without further splitting.

Fractionation [12] of cottonseed foots fatty acids is carried out on a commercial scale in the continuous column type of stills similar to those employed in petroleum refining. Relatively pure palmitic acid and a mixture of oleic and linoleic acids are produced.

Yields from continuous methods are greater than from the batch system and the quality of the distillate is superior. The short length of time during which fatty acids are exposed to heat and the lower operating temperature in the continuous system as compared with the batch method are perhaps the greatest factors in producing a superior distillate from the continuous still. Improvements in deaerating and applying heat to the stock being distilled have been made in a further effort to obtain a more stable product (Fig. 202).

C. Treatment of Distilled Fatty Acids

A successful method of treating distilled fatty acids for color and odor improvement has not yet been disclosed. The quality of distilled fatty acids is controlled mainly by the original quality and the pretreatment of the fatty acid feed stock, the method of distillation employed, and the number of redistillations.

In the case of cottonseed oil, the nature of the fatty acids can be altered by hydrogenation. This is done commercially as described by McKee and Graziani.[13] An intermediate fraction consisting mainly of

[9] J. W. Bodman (to William Garrigue & Co.), U.S. Pat. 1,372,477 (1921).
[10] S. Goranflo (to Wilson & Co., Inc.), U.S. Pat. 1,951,241 (1934).
[11] V. Mills (to Procter & Gamble Co.), U.S. Pat. 2,274,801 (1942).
[12] R. H. Potts and J. E. McKee (to Armour & Co.), U.S. Pat. 2,054,096 (1936) and later patents.
[13] J. E. McKee and O. Graziani (to Armour & Co.), U.S. Pat. 2,304,842 (1942).

oleic and linoleic acids, as produced from a fractionating column, is subjected to conventional hydrogenation with nickel catalyst at a temperature of about 250° C. (482° F.) in an atmosphere of hydrogen. The resulting product is a technically pure grade of stearic acid.[14] This product is not to be confused with commercial stearic acid, which is mainly a mixture of palmitic and stearic acids with somewhat more palmitic acid than stearic acid.

Straight-run cottonseed oil fatty acids are also subjected to hydrogenation. The resulting product [14] is a mixture of about 75% stearic acid and the balance mainly palmitic acid.

V. Products and Usages

A. Crude and Refined Oil

The use of cottonseed oil itself in nonedible products is rather limited, as was indicated in Table 202. Only a few million pounds of oil per year are consumed as such in nonedible products. Principal uses are in soap, lubricants, sulfonated oil, pharmaceuticals, protective coatings, rubber, and as a vehicle for nickel bearing catalysts. It is also used, to a lesser extent, in the manufacture of toilet articles, leather, textiles, printing ink, polishes, and synthetic plastics and resins.

A limited amount of cottonseed oil has been subjected to hydrogenation and the hardened product used as a substitute for palm oil in metal working industries.

B. Foots

The major portion of the foots recovered from the refining process is used directly in soap manufacture. Cottonseed oil foots are utilized as the entire soap base of highly alkaline washing powders. The saponification and washing of the foots is completed in the usual manner, and the kettle soap is mixed with soda ash and water in such proportions as to produce a washing powder containing from 4 to 45% anhydrous soap, the balance being hydrated soda ash. Figure 203 illustrates the spray tower method of manufacturing washing powders.

In conjunction with other soap bases, cottonseed foots are used in the manufacture of highly built, household powdered soap and yellow bar laundry soap. Soap made from cottonseed oil has good detergent properties, is mild in its action on the skin, and has good lathering qualities. Its chief disadvantage is a relatively poor keeping quality.

The balance of refinery foots is processed in fatty acid distillation plants for recovery of fatty acids and pitch.

[14] *Neo-Fat: Neo Fatty Acids and Oils for Industrial Uses,* Armour & Co., Chicago, 1945.

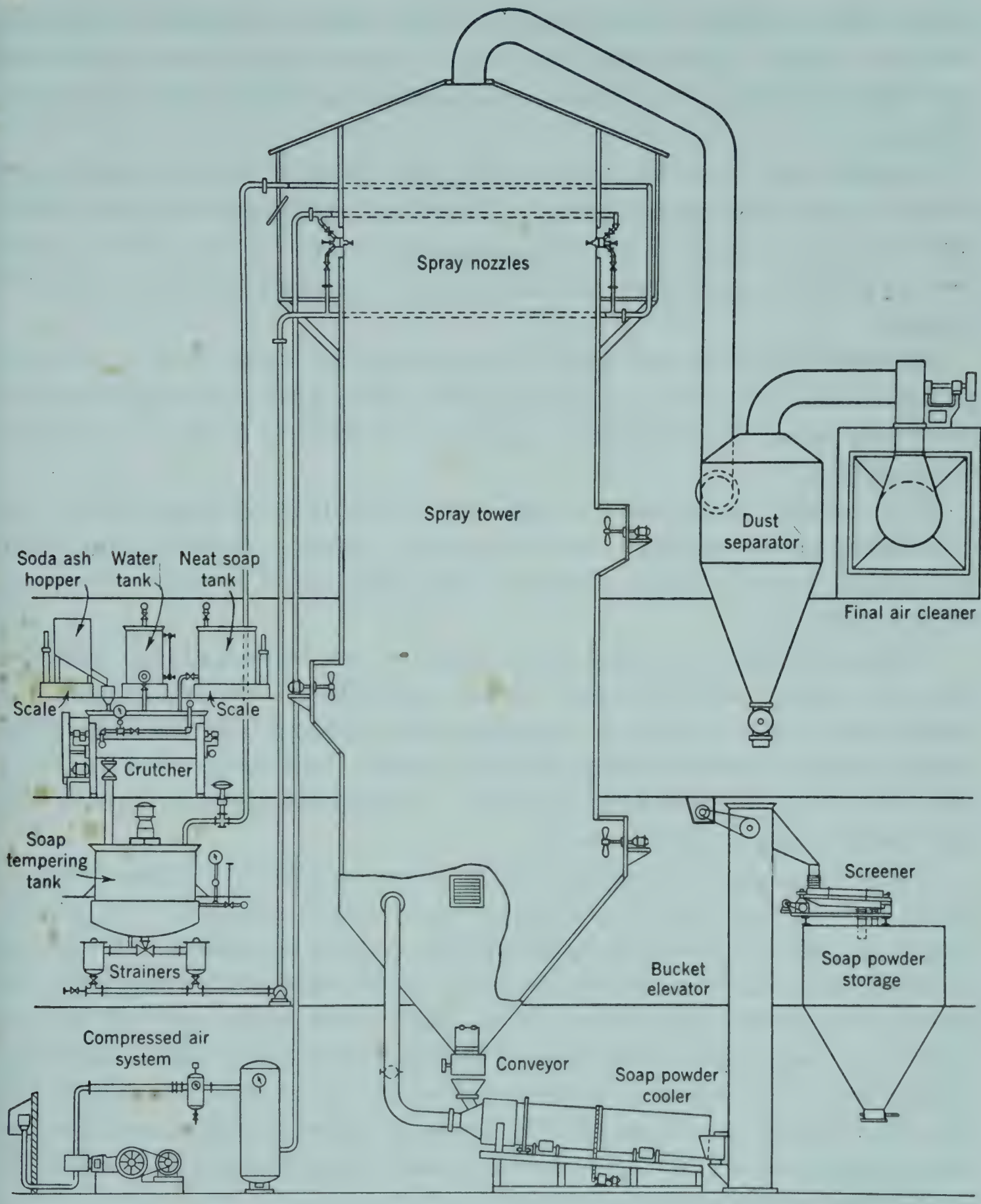


Fig. 203. Spray process system for washing powders.
(Courtesy *Wurster & Sanger, Inc.*)

C. Distilled Fatty Acids

The largest single user of distilled cottonseed fatty acids is the soap industry. Quality standards for the acids are not rigid. Generally, the fatty acids are double-distilled, or the equivalent, and light in color. In addition to the soap products for which foots are used regularly, the fatty acids are used in potash base paste and liquid soaps.

Cottonseed fatty acids are used to a large extent as an ingredient in

rubber compounding. In this field, they have largely replaced stearic acid. Hitherto, rubber compounded with the aid of unsaturated fatty acids had poor aging qualities. This defect has been overcome by the use of anti-oxidants.

Another large use of cottonseed oil fatty acids is in the manufacture of alkyd resins. The manufacture of lime-base cup grease and other lubricants consumes a large proportion of the cottonseed oil fatty acids. Minor uses for the fatty acids are much the same as those listed previously for the oil itself.

However, the fractionation of cottonseed oil foots fatty acids into palmitic and a mixture of oleic and linoleic acids plays an important part in a fairly recent development [14] centered around fatty acids as a chemical intermediate.

The chemical compounds manufactured in this development consist of uniform-length, long-chain amines, amides, nitriles, quarternary amine compounds, esters, alcohols, metallic salts, amine salts, ketones, and many other compounds.

These pure alkyl chemical compounds find use in such diverse applications as wetting and detergent agents, emulsifiers, modifying agents in plastics and resins, germicides, flatting agents in paints, ore flotation, plasticizing agents, waterproofing, bonding agents, and waxes, to mention a few. The field of application for these compounds appears to be in its embryonic stage of development.

Fatty acids from cottonseed oil foots are important in this development because they provide, through fractional distillation: (*a*) a pure source of palmitic acid for saturated alkyl chain compounds containing 16 carbon atoms, (*b*) a uniform source of mixed oleic and linoleic acids for slightly unsaturated 18 carbon atom alkyl compounds, and (*c*) a pure source of stearic acid for saturated 18 carbon atom alkyl compounds. The stearic acid is obtained by hydrogenation of the mixture comprising the oleic and linoleic acid fraction. The types of chemical compounds derived from cottonseed oil fatty acids are the same as those listed above and their applications are of the same nature.

Although the volume of production of fatty acid derivatives is not large in comparison with production in the entire fat and oil field, their applications in industry are important. Their development, based as it is on a cheap and abundant raw material, *e.g.*, refinery foots, provides a field for market research with interesting possibilities.

D. Cottonseed Pitch

The residue remaining after the volatile fatty acids have been removed from crude cottonseed fatty acids is termed "pitch." It consists of non-volatile fatty acids, polymerized fatty material, unsaponifiable materials

originally present in the feed stock, and other impurities not completely identified.

The pitch is a black, amorphous material having good waterproofing properties. It is used principally in special paints and varnishes, asphalt tile and roofing materials, and electrical wiring insulation requiring high resistance to moisture.

CHAPTER XXI

COTTONSEED AS A SOURCE OF ANIMAL FEEDSTUFFS

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I. Chemical Constituents as Related to Feeding Value

A. PROTEINS AND AMINO ACIDS

Cottonseed meal and cake have been highly esteemed as protein concentrates for livestock for many years. Although these products contain other substances of nutritional importance, their commercial value is due primarily to their protein content.

The nutritive value of the mixed proteins of cottonseed has been studied by the use of nitrogen balance tests as developed by Mitchell and coworkers, and also by feeding trials in which growth rates and efficiency of feed utilization were measured. The latter type of experiments differ from practical feed tests in that the proteins of the materials to be tested constitute practically the only source of protein in the rations. The investigations of Osborne and Mendel,[1] Nevens,[2] Braman,[3] Zucker and Zucker,[4] Smuts,[5] and Jones and Divine [6] all lead to the conclusion that the proteins of cottonseed are of high nutritional value. Osborne and Mendel [1] studied isolated cottonseed globulin and also the mixed proteins of cottonseed. The results of these experiments left no doubt as to the adequacy of cottonseed proteins for the growth of rats. In comparative rat feeding tests, Smuts [5] found that the proteins of cottonseed were equal to the proteins of peanut meal and superior to the proteins of sesame meal, copra meal, and lucerne meal (alfalfa meal) for the growth of these animals. In similar experiments, Jones and Divine [6] found that casein and the proteins of skim milk were superior to the proteins of oilseed flours, including cottonseed, soy-

[1] T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, **29,** 289–317 (1917).
[2] W. B. Nevens, *J. Dairy Sci.*, **4,** 552–588 (1921).
[3] W. W. Braman, *J. Nutrition,* **4,** 249–259 (1931).
[4] T. F. Zucker and L. Zucker, *Ind. Eng. Chem.*, **35,** 868–872 (1943).
[5] D. B. Smuts, *Onderstepoort J. Vet. Sci. Animal Ind.*, **10,** 193–205 (1938).
[6] D. B. Jones and J. F. Divine, *J. Nutrition,* **28,** 41 (1944).

bean, and peanut flour, when fed at a 9.1% protein level. The mixed proteins of cottonseed and wheat were better than the proteins of wheat alone.

It is known that the biological value of a protein, as determined by nitrogen balance studies, varies somewhat with the level of protein in the test ration. It is not surprising, therefore, to find some variation in the numerical values obtained by various workers for the biological value of the proteins of cottonseed meal. In spite of this difficulty, satisfactory agreement exists between the value of 78 reported by Braman [3] and the value of 81 found by Smuts and Malan.[7] The test ration used by Braman contained 1.349% nitrogen as compared to 1.5% in the ration used by the later workers. In experiments with rats, Bethke and co-workers [8] and also Braman [3] found that the proteins of linseed meal and cottonseed meal were equal both with respect to digestibility and biological value.

Mitchell and Hamilton [9] determined the digestibility and biological value of cottonseed meal proteins for hogs. The significantly lower biological value, 63, obtained in these tests was interpreted as indicating that the proteins of cottonseed meal are less efficiently utilized by hogs than by rats. Since hogs are particularly susceptible to the effects of gossypol, it is possible that these results were influenced by the gossypol content of the meal. The data of Lyman, Holland, and Hale,[10] with guinea pigs as test animals, shows that, even though the free gossypol content of cottonseed meal is low enough so that no symptoms of gossypol poisoning can be detected, the rate of growth of the animals may still be decreased.

Considerable variation exists in the values reported in the literature for the digestibility of the proteins of commercial cottonseed meal. It was shown by Lyman and Hale [11] that variations, such as the temperature, time, and moisture content, used in the manufacturing procedure can result in significant differences in the digestibility of cottonseed meal. It is well known that these processing factors in different mills are far from being uniform.

Gallup [12] showed that the apparent digestibility of the proteins of raw cottonseed, prepared by removing the oil and gossypol from the samples by extraction with ethyl ether, was higher than the digestibility of the proteins of commercial cottonseed meal. Autoclaving the meal resulted in a further decrease in digestibility.

[7] D. B. Smuts and A. I. Malan, *Anderstepoort J. Vet. Sci. Animal Ind.,* **10,** 207–219 (1938).
[8] R. M. Bethke, G. Bohstedt, H. L. Sassaman, D. C. Kennard, and B. H. Edington, *J. Agr. Research,* **36,** 855–871 (1928).
[9] H. H. Mitchell and T. S. Hamilton, *J. Agr. Research,* **43,** 743–748 (1931).
[10] C. M. Lyman, B. R. Holland, and F. Hale, *Ind. Eng. Chem.,* **36,** 188–190 (1944).
[11] C. M. Lyman and F. Hale, *unpublished experiments.*
[12] W. D. Gallup, *J. Biol. Chem.,* **76,** 43–53 (1928).

Olcott and Fontaine,[13, 14] in agreement with the earlier report of Osborne and Mendel,[1] found that heating cottonseed with steam under pressure significantly lowered the over-all nutritive value of the proteins. This treatment also lowered the solubility of the proteins in 3% sodium chloride solution.[14] In a limited number of experiments with commercial cottonseed meal samples, a correlation was found between the solubility of the proteins and their nutritive value. Protein solubility tests were suggested as an aid in processing control for the improvement of the feeding value of cottonseed meal. Further investigation of this problem is needed.

TABLE 205

Amino Acid Content of Cottonseed Meal[a]

Amino acid	Amount of the amino acid in cottonseed meal,[b] %	Amino acid in the protein,[c] %	Amino acid	Amount of the amino acid in cottonseed meal,[b] %	Amino acid in the protein,[c] %
Arginine	4.82	11.20	Lysine	1.78	4.15
Cystine	—	2.0[d]	Methionine	0.66	1.53
Glutamic acid	7.61	17.7	Phenylalanine	2.24	5.21
Glycine	1.90	4.42	Threonine	1.45	3.37
Histidine	1.14	2.65	Tryptophan	0.62	1.44
Isoleucine	1.70	3.95	Tyrosine	—	3.2[d]
Leucine	2.63	6.11	Valine	2.09	4.86

[a] Except as otherwise noted, values are from unpublished data of the authors.
[b] Cottonseed meal containing 43% protein.
[c] This is equivalent to calculating to 16% nitrogen.
[d] From R. J. Block and D. Bolling, *The Amino Acid Composition of Proteins and Foods*, C. C Thomas, Springfield (Ill.), 1945, p. 305.

The extent to which the proteins of raw soybeans are utilized by animals can be considerably improved by a suitable heat treatment. The situation with respect to cottonseed is quite the contrary, since there is no indication that any degree of heat treatment improves the utilization of cottonseed proteins. An explanation for the effect of heat on raw soybeans is offered by the recent work of Ham and associates.[15] These investigators discovered that the raw beans contain a proteolytic enzyme inhibitor. Unless this inhibitor is destroyed by heat, it interferes with the digestion process so that the soybean proteins cannot be fully utilized.

One of the possibilities with respect to the solvent-extraction method for the processing of cottonseed is that the procedure may be worked out in such a manner that the proteins in the meal will be left in a more digestible form.

The distribution of the essential amino acids is undoubtedly one of the

[13] H. S. Olcott and T. D. Fontaine, *J. Nutrition*, **22**, 431–437 (1941).
[14] H. S. Olcott and T. D. Fontaine, *Ind. Eng. Chem.*, **34**, 714–716 (1942).
[15] W. E. Ham, R. M. Sandstedt, and F. E. Mussehl, *J. Biol. Chem.*, **161**, 635–642 (1945).

most important factors in determining the nutritive value of proteins. Table 205 shows the amino acid composition of cottonseed meal except for a few of the amino acids for which data is not yet available. These data [16] were obtained by the use of microbiological methods developed in the authors' laboratory,[17-19] except as otherwise indicated.[20]

Additional data on the proteins of cottonseed will be found in Chapter VIII.

B. Vitamin and Mineral Content of Cottonseed Meal

Cottonseed meal is a good source of the B vitamins including thiamin, niacin, pantothenic acid, and riboflavin. The removal of the oil, by the milling of cottonseed, concentrates the water-soluble vitamins in the protein cake so that cottonseed meal or cake is richer in these vitamins than whole cottonseed or even the hulled kernels. This is in marked contrast to what happens during the milling of wheat for the manufacture of flour. The manufacture of flour results in the removal of a large percentage of the water-soluble vitamins along with the outer coatings of the grain.

TABLE 206

Vitamin and Mineral Content of Cottonseed Meal[a]

Vitamin	Content, mg. per lb.	Mineral	Content, g. per lb.
Riboflavin	4.08	Calcium	0.86
Pantothenic acid	6.35	Phosphorus	5.04
Niacin	20.40	Sodium	0.18
Thiamin	6.13	Potassium	6.63
		Manganese	0.00820

[a] Data from U.S. Dept. Agr. Animal Husbandry Division Report No. 2 (1937) and No. 61 (1943); U.S. Dept. Agr., *Yearbook*, 1939, pp. 481, 1067.

Cottonseed meal contains very little of either vitamin A or D.

As compared to other vegetable protein concentrates or the grains, cottonseed meal is relatively high in phosphorus content. A large percentage of this phosphorus is in the form of phytin. According to the recent work of Boutwell and associates,[21] phytin phosphorus can be utilized by animals provided that the ration contains ample vitamin D.

[16] C. M. Lyman and F. Hale, *unpublished experiments.*

[17] K. A. Kuiken, W. H. Norman, C. M. Lyman, and F. Hale, *Science,* **98,** 266–268 (1943).

[18] C. M. Lyman, K. A. Kuiken, L. Blotter, and F. Hale, *J. Biol. Chem.,* **157,** 395–405 (1945).

[19] K. A. Kuiken, W. H. Norman, C. M. Lyman, F. Hale, and L. Blotter, *J. Biol. Chem.,* **151,** 615–626 (1943).

[20] R. J. Block and D. Bolling. *The Amino Acid Composition of Proteins and Foods.* C. C Thomas, Springfield (Ill.), 1945, p. 305.

[21] R. K. Boutwell, R. P. Geyer, A. W. Halverson, and E. B. Hart, *J. Nutrition,* **31,** 193–202 (1946).

Average values for the content of vitamins and some of the minerals of cottonseed meal are given in Table 206.

C. Relationship of Gossypol to Feeding Value of Cottonseed Meal

Some years ago, it was a common belief that cottonseed meal and raw cottonseed caused blindness, stiffness of gait, swelling of the joints, and loss of appetite in cattle. At one time, these effects were attributed to gossypol. However, the symptoms were strikingly like those of vitamin A deficiency and it is now well established that the disease was actually due to a lack of this vitamin and not to anything contained in cottonseed or cottonseed meal. The results of a number of investigations [22-26] give adequate proof in support of this conclusion.

Although cattle can consume large quantities of raw cottonseed continuously for a long period of time without the slightest indication of any ill effect (see, for example, page 67), rabbits, guinea pigs, and swine will die within a short time if they eat very much of it. Withers and Carruth [27] studied this problem from the chemical viewpoint. They isolated the compound known as gossypol (discovered by Marchlewski in 1899) and studied the effect of this substance on experimental animals. Withers and Carruth,[27] and others [28] have shown that purified gossypol has a poisonous effect similar to that of raw cottonseed when fed to rabbits, rats, guinea pigs, and swine.

During the processing of cottonseed by the hydraulic or expeller procedure, the "cooking" or moist heat treatment causes changes to take place in the material which largely inactivates the gossypol. Withers and Carruth [29] postulated that the changes involved an oxidation of the gossypol molecule and named the supposed decomposition product "d" gossypol. Sherwood [30] thought that an hydrolysis instead of an oxidation took place. Later Clark [31] presented evidence to show that the chemical structure of the gossypol molecule is not altered by conversion to the inactive or "d" gossypol form. However, solubility relationships were changed. It was postulated that the inactivation of the gossypol was due to a combination of the gossypol with some of the cottonseed protein. This would involve a

[22] L. A. Moore and C. F. Huffman, *Am. Soc. Animal Prod. Proc. 25th Ann. Meeting,* pp. 150–152 (1931).
[23] O. E. Reed, C. F. Huffman, and L. H. Addington, *J. Dairy Sci.,* **11,** 488–507 (1928).
[24] J. O. Halverson and F. W. Sherwood, *North Carolina Agr. Expt. Sta. Tech. Bull.,* **39** (1930).
[25] R. E. Dickson, J. K. Riggs, and B. T. Marion, *Texas Agr. Expt. Sta. Ann. Rept.,* **1940,** 202.
[26] A. H. Kuhlman, E. Weaver, and W. D. Gallup, *Oklahoma Agr. Expt. Sta. Ann. Rept. 1936–38,* **1939,** pp. 67–68.
[27] W. A. Withers and F. E. Carruth, *J. Agr. Research,* **5,** 261–288 (1915).
[28] E. W. Schwartze and C. L. Alsberg, *J. Agr. Research,* **28,** 173–189 (1924).
[29] W. A. Withers and F. E. Carruth, *J. Agr. Research,* **12,** 83–102 (1918).
[30] F. W. Sherwood, *J. Agr. Research,* **32,** 793–800 (1926).
[31] E. P. Clark, *J. Biol. Chem.,* **76,** 229–235 (1928).

reaction of free amino groups on the protein molecule with the carbonyl group of gossypol. On the basis of this interpretation, inactivated gossypol is often referred to as "bound" gossypol.

To gain further evidence regarding Clark's hypothesis, Lyman [32] prepared a compound of casein and gossypol by heating moist casein with pure gossypol dissolved in refined cottonseed oil. The gossypol could not be removed from the product by lengthy extraction with ethyl ether and other solvents, but could be removed by the use of aniline in the same manner that "d" gossypol can be removed from cottonseed meal. This experiment was interpreted as evidence in favor of Clark's bound gossypol theory.

The amount of free or unchanged gossypol in commercial cottonseed meal, while almost always relatively small in comparison with raw cottonseed, shows considerable variation from sample to sample.

Methods of treating commercial cottonseed meal, including the use of chemicals, for the purpose of removing any possible residual harmful qualities have received the attention of numerous investigators. Soluble iron salts [33-37] have been used both to treat the meal and as additions to the rations. These studies indicate that the tolerance of swine and guinea pigs for gossypol can be greatly increased by the use of a soluble form of iron. It was shown by Withers and Carruth [27] that gossypol and iron form an insoluble complex. The most logical explanation as to the mode of action of iron is that the formation of this complex prevents the gossypol from being absorbed from the digestive tract. In the case of chickens, evidence for this has been obtained by Swenson, Fieger, and Upp.[38] Gallup and Reder [39] reported beneficial effects from the use of sodium and calcium salts in connection with cottonseed meal. The use of any chemical for counteracting the effect of gossypol has the objection that it takes on the nature of an antidote rather than solving the problem at its source.

As early as 1917, Osborne and Mendel [40] reported that the toxicity of raw cottonseed was progressively reduced by steaming. Treating commercial cottonseed meal by steaming, autoclaving,[41-44] or cooking with

[32] C. M. Lyman, *unpublished experiments.*
[33] W. A. Withers and J. F. Brewster, *J. Biol. Chem.*, **15,** 161–166 (1913).
[34] W. A. Withers and F. E. Carruth, *J. Biol. Chem.*, **32,** 245–257 (1917).
[35] J. P. McGowan and A. Crichton, *Biochem. J.*, **18,** 273–282 (1924).
[36] W. D. Gallup, *J. Biol. Chem.*, **77,** 437–449 (1928).
[37] W. L. Robinson, *Ohio Agr. Expt. Sta. Bull.*, **534** (1934); *Am. Soc. Animal Prod. Proc. 29th Ann. Meeting,* pp. 87–91 (1936).
[38] A. D. Swenson, E. A. Fieger, and C. W. Upp, *Poultry Sci.*, **21,** 374–378 (1942).
[39] W. D. Gallup and R. Reder, *Proc. Oklahoma Acad. Sci.*, **14,** 74–75 (1934); *J. Agr. Research,* **52,** 65–72 (1936).
[40] T. B. Osborne and L. P. Mendel, *J. Biol. Chem.*, **29,** 289–317 (1917).
[41] I. G. Macy and L. B. Mendel, *J. Pharmacol.*, **16,** 345–390 (1920).
[42] C. T. Dowell and P. Menaul, *J. Agr. Research,* **26,** 9–10 (1923).
[43] W. D. Gallup, *Ind. Eng. Chem.*, **19,** 726–728 (1927); *J. Dairy Sci.*, **9,** 359–372 (1926).
[44] B. Hassel, *Seifensieder-Ztg.*, **57,** 52–53 (1930).

water [40, 45] has recently been investigated and advocated by some research workers.

For the proper interpretation and correlation of the results of investigations of this kind, it is necessary that the differences in sensitivity of different animals to the effects of gossypol be fully recognized. It has already been mentioned that cattle can consume large quantities of even raw cottonseed without any detectable ill effects. This is also true of sheep. Rabbits, swine, and guinea pigs are extremely sensitive, while rats and chickens are intermediate in their reaction and can withstand quantities of gossypol which would be injurious to guinea pigs, rabbits, or swine. The difference in sensitivity between rats and pigs is evident from the work of Bethke and associates [8] who fed identical rations to the two kinds of animals.

Lyman, Holland, and Hale [46] have shown that by controlling the processing variables—temperature, time, and moisture content—cottonseed meal can be manufactured which will not cause injury of any kind to guinea pigs or to swine even when fed at a level of 25% of the total ration for a considerable length of time. The process does not involve the addition of any chemicals nor is any additional step necessary in the milling procedure. Somewhat more moisture is necessary than is used by the average mill. By repeated processing tests with different batches of seed, it was established that the procedure as described would always give these results. The method was tested not only with experimental laboratory equipment, but also in a commercial oil mill.

Cottonseed meal made by this method has a very low-free gossypol content, usually running about 0.02%, as determined by the colorimetric procedure of Lyman, Holland, and Hale.[47] The simplicity of the colorimetric method makes it useful for processing control when it is desired to manufacture meal of low free gossypol content.

Using this colorimetric method, a close correlation was found between the free gossypol content of several series of experimental cottonseed meal samples and the severity of deleterious effects in guina pig feeding tests. These findings added further evidence in favor of the conclusion of previous workers that gossypol is the chemical substance primarily involved in this problem.

In considering the relationship of gossypol to the practical feeding value of cottonseed meal, it is to be remembered that any commercial cottonseed meal as it is made at this time can be safely fed to hogs provided the amount is limited to 9% of the total ration. This fact has been

[45] W. E. Sewell, *Alabama Polytech. Inst. Agr. Expt. Sta. Bull.*, **259** (1943).
[46] C. M. Lyman, B. R. Holland, and F. Hale, *Ind. Eng. Chem.*, **36**, 188–190 (1944).
[47] C. M. Lyman, B. R. Holland, and F. Hale, *Ind. Eng. Chem., Anal. Ed.*, **15**, 489–491 (1943).

established by Hale [48] and verified by others.[49] The use of cottonseed meal in practical rations for livestock and poultry is discussed in the latter portion of this chapter.

D. Cottonseed Meal and the Storage Quality of Eggs

Although cottonseed meal is a good source of protein for poultry rations, it is not recommended for laying hens if the eggs are to be kept in cold storage. Eggs from hens which have been fed cottonseed meal usually appear perfectly normal when first laid, but after several weeks of storage under the usual commercial conditions a discoloration begins to develop, particularly in the yolks, which soon makes the eggs unsalable. Some investigators have found that if sufficiently large quantities of cottonseed meal are fed the discoloration may appear in the fresh eggs before they are a week old. It is probable that the nutritive value of eggs which become discolored in this manner is not affected in any way.

The abnormalities which occur in these eggs are somewhat variable. The following conditions are typical. The yolks may be olive green or almost black. In other cases, there is no trace of the dark green color but the yolks are reddish instead. A mottled condition is common. The yolks may or may not be abnormally large. A thick gelatinous consistency of the yolks is usually found. Several workers have described a pink or almost red color of the whites.

Investigations on this problem date back to 1891, when Roberts and Rice [50] noted that discolored egg yolks were produced by hens fed rations containing cottonseed meal. In 1918, Thompson [51] reported that spotted eggs were produced as a result of feeding cottonseed meal. Several subsequent reports have come from the New Mexico group.[52, 53] As a result of a systematic study of the effect of rations containing cottonseed meal on the storage quality of eggs, Sherwood [54] concluded that the cause of the deterioration of the eggs on storage was some substance associated with crude cottonseed oil. It now appears that two distinct chemical substances are involved. The investigations of Schaible, Moore, and Moore,[55] Lorenz,[56] and Swenson, Fieger, and Upp [38] all support the conclusion that the olive green-colored yolks are caused by the gossypol in cottonseed meal.

[48] F. Hale, *Texas Agr. Expt. Sta. Bull.*, **410** (1930).
[49] Wm. J. Loeffel, *Univ. Nebraska Circ.*, **No. 40,** 29 (1932).
[50] I. P. Roberts and J. E. Rice, *Expt. Sta. Record,* **2,** 506–507 (1891).
[51] R. B. Thompson, *New Mexico Agr. Expt. Sta. Bull.*, **117,** 16 (1918).
[52] *New Mexico Agr. Expt. Sta. Ann. Repts.*, **37,** 51–53 (1925–1926); **38,** 63–65 (1926–1927); **39,** 55–56 (1927–1928).
[53] A. L. Walker, L. N. Berry, and E. E. Anderson, *New Mexico Agr. Expt. Sta. Bull.*, **177** (1929).
[54] R. M. Sherwood, *Texas Agr. Expt. Sta. Bull.*, **376** (1928); **429** (1931).
[55] P. J. Schaible, L. A. Moore, and J. M. Moore, *Poultry Sci.*, **12,** 334 (1933).
[56] F. W. Lorenz, *Poultry Sci.*, **18,** 295–300 (1939).

Lorenz [56] found that the gelatinous consistency of the yolks as well as the olive green color is due to gossypol. It was reported [57] that pink whites, reddish-colored yolks, and abnormally large yolks were produced by feeding, besides cottonseed, other malvaceous plants—plants which do not contain any gossypol. These characteristics were also produced by feeding small amounts of summer yellow cottonseed oil from which all gossypol had been removed by the refining process. The substance which causes the pink or reddish discoloration of both whites and yolks, and the abnormal enlargement of the yolks appears to be either identical or closely associated with the substance which gives the Halphen reaction.

The chemical mechanism by which gossypol causes the olive green-colored yolks has been studied by Swenson, Fieger, and Upp.[38] Evidence was presented to show that the iron which is normally bound by the egg yolk proteins is released during storage and that this iron combines with gossypol to form the product which is responsible for the dark color of the egg yolks.

A test for detecting potentially olive-colored yolks in fresh eggs has been described by Schaible, Moore, and Moore.[58] When fresh eggs are broken in an atmosphere of ammonia, the yolks of the eggs which are capable of developing the olive green color change to a chocolate brown in a very short time. The chocolate brown color is probably the ammonium salt of the iron–gossypol complex.

When iron salts are fed with cottonseed meal, at least a partial protection against discoloration of the eggs is afforded. It has been shown [38] that the iron salts tend to prevent the absorption of the gossypol during the process of digestion.

E. Effect of Feeding Cottonseed Products on the Quality of Butter

When green pasture constitutes the chief food for dairy cattle, the keeping quality of the butter is relatively poor. Likewise, the melting point of the butter is low enough to make it difficult to handle in warm climates. Eckles and Palmer [59] have shown that supplementing green pasture with cottonseed meal results in butter of better keeping qualities and butter which stands up better at summer temperatures.

The feeding of excessive amounts of cottonseed meal or cake to dairy cattle may, under certain conditions, result in undesirable changes in the physical and chemical constants of the butterfat and in the properties of the butter. Such butter has been frequently characterized as having a

[57] F. W. Lorenz and H. J. Almquist, *Ind. Eng. Chem.*, **26** 1311–1313 (1934).
[58] P. J. Schaible, J. A. Moore, and J. M. Moore, *Science*, **79**, 372 (1934).
[59] C. H. Eckles and L. S. Palmer, *Missouri Agr. Expt. Sta. Research Bull.*, **27** (1916).

gummy texture [59-63] and as being too hard or firm of body. The flavor has been described as being somewhat flat. These conclusions have been largely drawn from experiments in which large amounts of cottonseed meal were fed. The following quotation [60] is taken from the 30th Annual Report of the South Carolina Experiment Station: "Cottonseed meal products, if fed moderately as they should be, do not produce sticky or gummy butter."

The changes in the physical and chemical properties [59, 63-65] of butter which are inclined to take place as a result of feeding cottonseed meal, are as follows: (*a*) increase in the melting point, (*b*) decrease in the content of volatile fatty acids, (*c*) increase in iodine number, (*d*) decrease in saponification value, and (*e*) decrease in Reichert-Meissl number. The extent of these changes is dependent not only on the amount of cottonseed meal fed, but also on several other factors including the oil content of the meal and the nature of the other constituents of the ration.

Eckles and Palmer [59] found that the typical characteristics of cottonseed meal butter were produced by feeding cottonseed oil as well as the meal, and that the effect of the meal could be accounted for on the basis of its oil content. The effects of feeding cottonseed meal were most pronounced when fed with dry feeds, such as timothy hay, corn stover, cottonseed hulls, or alfalfa hay. Feeding a liberal ration of corn silage along with the cottonseed products resulted in minimizing the effects of the meal.

Available information concerning the role of ingested fat in the formation of milk is too limited to offer a complete explanation concerning the effects of cottonseed oil on butter fat. At ordinary temperatures, cottonseed oil is a liquid, yet it exerts a hardening effect on the butter. However, cottonseed oil is relatively high in its content of saturated fatty acids, hence it appears that there may be a selective utilization of these acids during the process of milk formation.

II. Use of Cottonseed Meal in Rations for Livestock and Poultry

A. Forms of Cake and Meal

Cottonseed cake as it comes from the press is either ground and sold as cottonseed meal, or is cracked and screened into the following sizes to meet the various requirements of the livestock feeding industry:

[60] *South Carolina Expt. Sta. 30th Ann. Rept.*, p. 16 (1917).
[61] J. I. Keith, A. H. Kuhlman, E. Weaver, and W. D. Gallup, *Oklahoma Agr. Expt. Sta. Repts.*, pp. 162–163 (1930–1932).
[62] J. I. Keith, A. H. Kuhlman, E. Weaver and W. D. Gallup, *Oklahoma Agr. Expt. Sta. Repts.*, pp. 164–166 (1932–1934).
[63] E. W. Neasham and A. J. Gelpi, *Natl. Butter Cheese J.*, **25,** No. 1, 12–13 (1934).
[64] H. H. Harrington and D. Adriance, *Texas Agr. Expt. Sta. Bull.*, **29** (1893).
[65] O. F. Hunziker, H. C. Miller, and G. Spitzer, *Indiana Agr. Expt. Sta. Bull.*, **159,** 308–312 (1912).

1. *Nut-size cake* which will pass through 1½-inch round perforation and over ¾-inch round perforation.

2. *Sheep-size cake* which will pass through ⅞-inch round perforation and over ⅝-inch round perforation.

3. *Pea-size cake* which will pass through ⅝-inch perforation and over ⅜-inch round perforation.

4. *Pebble-size cake* is a product consisting of fine particles and small pieces of cottonseed cake capable of passing through ⅜-inch round perforation.

In order to meet a demand from the range cattle and sheep raisers, many of the cotton oil mills are now offering cubed or pelleted cottonseed cake.

Cubes are being prepared in two sizes, namely, a large size to compare with nut-size cake, and a smaller size to compare with sheep-size cake. The dimensions of the large-size cake cubes are usually ⅞ inch by 1¼ to 1½ inches. The smaller or sheep-size cube measures ⅝ inch by ½ to ¾ inch.

The product commonly called pelleted cake is that which is made with a round die instead of a square die—the latter is used for the cubes. The pellets that compare with the nut-size cake measure ¾ to ⅞ inch in diameter and about 1 to 1½ inches in length. The sheep-size pellet measures ½ to ⅝ inch in diameter. The pea-size measures about ⅜ inch in diameter by ¾ to 1 inch long.

Many cattlemen and sheepmen prefer the cubed or pelleted cake to the cracked nut- or sheep-size cake because of the uniformity in size, and also the fact that the cubes and pellets are relatively soft. The analysis of cottonseed cake cubes and pellets is identical with that of the cracked cottonseed cake.

The cracked cottonseed cake or the cubes and pellets may be fed on good turf or clean firm ground to range cattle and sheep. Troughs for feeding are sometimes used where snow covers the range.

The cake is ground into cottonseed meal for use in mixed rations, such as may be used for lot feeding to beef or dairy cattle, sheep, horses, swine, and poultry.

In the following pages the practical feeding of cottonseed meal to different kinds and classes of animals will be considered in detail, since optimum feeding methods vary widely, according to the kind and condition of the animal, as well as the particular effects desired.

B. Feeding of Beef Cattle

Many beef cattle investigations conducted by experiment stations have been concerned with the value of cottonseed meal and cake as protein

supplements in all phases of beef production, and also the value of cottonseed hulls as a roughage.

On the range, cottonseed meal and cake are used extensively to supply the needs of the breeding herd for protein and phosphorus. In work done at the Montana Station, Black and co-workers [66] showed that 1 pound of cottonseed cake fed on the range to mature beef cows during the winter replaced 10 pounds of hay fed in the feedlot. Lantow,[67] of New Mexico, compared the value of cottonseed cake and ground yellow corn for the supplemental feeding of cows and weaned calves on the range. He found that 1 pound of cottonseed cake fed daily to brood cows increased their weights in the spring, that they produced a larger calf crop, and that the calves weaned at heavier weights from cows that had received supplemental feeding during the winter. Watkins,[68] at the New Mexico Station, found that the feeding of cottonseed cake to cattle on the range receiving a feed low in protein increased the digestibility of all the nutrients in the low-protein feed, and he concluded that the protein added to a ration with an extremely wide nutritive ratio was solely responsible for the increase in the total digestible nutrients.

Bray,[69] at the Louisiana Station, found that, by feeding a mixture of equal parts of corn chops or rice bran and cottonseed meal to calves before weaning, he could increase their weights at the end of a 4½-month feeding period by 50 pounds. Blizzard,[70] of Oklahoma, found that feeding varying amounts of cottonseed meal in calf fattening rations, 2½ pounds per calf per day, produced more bloom, better coats of hair, and as a result, may add to the selling price of the calves. This work also showed that cottonseed meal was as much as 102% more valuable than ground shelled corn in an alfalfa hay ration for fattening calves.

Jones and co-workers,[71] in Texas, found that supplementing of Sudan grazing with liberal amounts of cottonseed cake increased the rate of gain of yearling steers about ⅓ pound per head daily; the added weight lessened, by 30 days, the time required for finishing in the dry lot. Grimes *et al.*,[72] at the Alabama Station, in finishing steers for the June market, found that 4.5 pounds of cottonseed cake or meal fed on grass increased the rate of gain as much as 0.6 pound per head per day. That heavy feeding of cottonseed meal to yearling steers produced excellent gains over a long feeding period when steers were receiving alfalfa hay

[66] W. H. Black, J. R. Quesenberry, and A. L. Baker, *U.S. Dept. Agr. Tech. Bull.*, **603** (1938).
[67] J. L. Lantow, *New Mexico Agr. Expt. Sta. Bull.*, **202** (1932).
[68] W. E. Watkins, *New Mexico Agr. Expt. Sta. Bull.*, **194** (1931).
[69] C. I. Bray, *Louisiana Agr. Expt. Sta. Bull.*, **249** (1934).
[70] W. L. Blizzard, *Oklahoma Agr. Expt. Sta. Bull.*, **237** (1939).
[71] J. H. Jones, R. A. Hall, J. M. Jones, and W. H. Black, *Texas Agr. Expt. Sta. Bull.*, **564** (1938).
[72] J. C. Grimes, W. E. Sewell, and G. J. Cottier, *Alabama Agr. Expt. Sta. Circ.*, **No. 72** (1935).

and silage was proved by Knox and Neale,[73] at the New Mexico Station. At the Colorado Station, Osland *et al.*[74] found that feeding 3 pounds of cottonseed meal daily per head to mature steers on a ration of wet beet pulp, beet molasses, and alfalfa hay increased the gain 0.9 pound per head per day, and reduced the unit cost of gains. Skinner and King,[75] at the Purdue Station, conducted a series of tests for many years on the feeding of cottonseed meal to fattening cattle, and stated that the rate of gain and selling price of the cattle are increased by the addition of cottonseed meal, and the animals were easier to keep on feed than those not fed a protein supplement. Workers at the Oklahoma Experiment Station [76] found that supplements of cottonseed cake improved the digestibility of both winter grass and prairie hay rations.

For finishing mature steers in the feedlot, Buchanan,[77] at the Mississippi Station, found that 100 pounds of cottonseed hulls was equal to 272 pounds of sorghum silage in feeding value. At the South Carolina Station, Godbey and Starkey [78] compared rations of cottonseed meal and hulls with corn and alfalfa hay for fattening steers. The concentrates were fed at the rate of 1 pound per 100 pounds of live weight, and it was found that the steers on cottonseed meal and hulls gained 2.22 pounds per head daily, compared with 2.1 pounds for steers on alfalfa hay and corn. Less meal was required per unit of gain than the amount of corn required to produce the same gain. In a comparison of cottonseed meal and hulls with lespedeza hay and corn, steers received, in addition to the roughage, 1 pound of cottonseed meal or corn per 100 pounds of live weight daily in respective lots until they had gained 200 pounds. The cattle on meal and hulls gained faster and made cheaper gains than those on corn and lespedeza hay. Experiments such as these have proved that fattening cattle, carrying a reserve supply of carotene in their body fat as a source of vitamin A, while in the feedlot on a vitamin A-deficient ration can be fed on a meal and hull mixture with excellent results for 75 to 100 days.

That 100 pounds of cottonseed hulls were equal to feeding value to 218 pounds of sorghum silage was found by Means,[79] of Mississippi, when 5 to 7 pounds of cottonseed meal and 3 pounds of Johnson grass hay were fed to mature steers, in addition to the silage or hulls. In studying the comparative value of cottonseed hulls and sorghum silage for fattening

[73] J. H. Knox and P. E. Neale, *New Mexico Agr. Expt. Sta. Bull.*, **262** (1939).
[74] H. B. Osland, E. J. Maynard, and G. E. Morton, *Colorado Agr. Expt. Sta. Bull.*, **422** (1936).
[75] J. H. Skinner and F. G. King, *Purdue Agr. Expt. Sta. Bull.*, **433** (1938).
[76] C. S. Hobbs, W. D. Gallup, and B. R. Taylor, *J. Animal Science*, **4**, 395–402 (1945).
[77] D. S. Buchanan, *Mississippi Agr. Expt. Sta. Bull.*, **278** (1930).
[78] E. G. Godbey and L. V. Starkey, *South Carolina Agr. Expt. Sta. Ann. Rept.*, p. 86 (1939).
[79] R. H. Means, *Mississippi Agr. Expt. Sta. Bull.*, **301** (1933).

yearling steers, Stangel and Reed,[80] at Texas Technological College, found that the hulls were 226% more valuable than sorghum silage, pound for pound, when each were fed in a ration of 4 pounds of cottonseed meal, grain, and enough alfalfa hay to supply vitamin A. Blizzard [70] found that, for fattening calves, 1 ton of cottonseed hulls is equal in feeding value to 1.43 tons of silage, or 330 pounds of corn, or 82 pounds of cottonseed cake.

Like many other roughages, cottonseed hulls lack vitamin A, so that it is advisable to supplement hulls with a source of vitamin A when they are fed over an extended period.

1. Vitamin A Deficiency

A condition which has been variously called "cottonseed meal poisoning," or "mealiness" is known to occur among cattle limited to such rations as cottonseed meal, cottonseed hulls, and white corn or other white grains. This condition has been identified as a vitamin A deficiency, and is not caused by any so-called poisonous substance in cottonseed meal or other feeds.[25]

This condition is characterized in the early stages by night blindness. In later stages, the cattle become less alert, and develop watering at the eyes, a nasal discharge, swelling at the joints, rapid respiration, a staggering gait, convulsions, loss of appetite, and finally complete blindness.[81]

In feeding rations low in vitamin A potency, such as cottonseed meal and cottonseed hulls only—or white grains, cottonseed meal, and low-grade weathered roughages—vitamin A supplements are apparently not needed for the first 50 to 80 days, except in the case of young calves which should receive a vitamin A supplement from the beginning of the feeding period. To guard against any occurrence of vitamin A deficiency, the cattle should be fed from 1 to 2 pounds of good quality leafy, green alfalfa hay per head daily, in addition to the regular rations.

2. Rations for Wintering the Farm Herd [82]

One to three pounds daily per head, of cottonseed meal or cake and limited amounts of silage, will carry cattle through the winter at small cost. The listings on page 840 are practical rations (figures are expressed in pounds) for wintering cattle.

Cattle of all ages should have salt and water available at all times, and should receive $\frac{1}{10}$ pound of ground limestone, bone meal, or oyster shell flour daily per head, unless legume hay is fed.

[80] W. L. Stangel and J. R. Reed, *Texas Tech. College Cattle Feeding Project No. 5* (1941).

[81] G. W. Barnes, A. L. Smith, and J. H. Jones, *Texas Ext. Circ.*, **No. 171** (1941).

[82] A. L. Ward, R. W. Wilson and W. P. Moore, National Cottonseed Products Association, *Feeding Practices,* 1940.

BREEDING COWS

Number 1		Number 4	
Silage	40–50	Prairie or grass hay	15
Cottonseed meal	1–2	Cottonseed hulls	5
Number 2		Cottonseed meal	1–2
Silage	25	**Number 5**	
Hay or cottonseed hulls	7–10	Legume hay	5
Cottonseed meal	2	Grass hay or cottonseed hulls	15
Number 3		Cottonseed meal	2
Pea vine, soybean or legume hay	5	**Number 6**	
Cottonseed hulls	10	Sorghum fodder	18
Cottonseed meal	3	Cottonseed meal	1–2

YEARLINGS OR TWO-YEAR-OLDS

Number 1		Number 2	
Silage	20	Legume or mixed hay	8
Hay or cottonseed hulls	10	Cottonseed hulls	10
Cottonseed meal	2	Cottonseed meal	1½

CALVES

Number 1		Number 2	
Silage	20	Hay or sorghum fodder	10
Hay or cottonseed hulls	5	Cottonseed hulls	5
Cottonseed meal	1½	Cottonseed meal	1½

3. Rations for 350- to 500-Pound Calves [83]

Each animal should receive 1/10 pound of a calcium supplement per day, with any ration used. Five alternative rations are given.

Constituent of ration	Amount, pounds				
	No. 1	No. 2	No. 3	No. 4	No. 5
First Four Weeks					
Ear corn chops or grain sorghum head chops	0	5	0	5	0
Corn chops or sorghum grain chops	4	0	0	0	4
Coarsely ground wheat or barley	0	0	4	0	0
Cottonseed meal	2	2	1½	2	1¾
Silage	24	0	12	0	0
Cottonseed hulls	0	0	4	8	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	8	0	0	0
Ground grain sorghum fodder	0	0	0	0	8
Second Four Weeks					
Ear corn chops or grain sorghum head chops	0	7	0	7	0
Corn chops or sorghum grain chops	6	0	0	0	6
Coarsely ground wheat or barley	0	0	6	0	0
Cottonseed meal	2	2	1½	2	1¾
Silage	24	0	12	0	0
Cottonseed hulls	0	0	4	7	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	8	0	0	0
Ground grain sorghum fodder	0	0	0	0	8

[83] A. L. Ward and R. W. Wilson, National Cottonseed Products Association, *Feeding Practices*, 1946

Constituent of ration	Amount, pounds				
	No. 1	No. 2	No. 3	No. 4	No. 5
Third Four Weeks					
Ear corn chops or grain sorghum head chops	0	9	0	9	0
Corn chops or sorghum grain chops	8	0	0	0	8
Coarsely ground wheat or barley	0	0	8	0	0
Cottonseed meal	2	2	1½	2	1¾
Silage	22	0	10	0	0
Cottonseed hulls	0	0	4	6	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	7	0	0	0
Ground grain sorghum fodder	0	0	0	0	7
Fourth Four Weeks					
Ear corn chops or grain sorghum head chops	0	11	0	11	0
Corn chops or sorghum grain chops	10	0	0	0	10
Coarsely ground wheat or barley	0	0	10	0	0
Cottonseed meal	2	2	1½	2	1¾
Silage	20	0	10	0	0
Cottonseed hulls	0	0	4	5	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	6	0	0	0
Ground grain sorghum fodder	0	0	0	0	6
Fifth Four Weeks					
Ear corn chops or grain sorghum head chops	0	13	0	13	0
Corn chops or sorghum grain chops	12	0	0	0	12
Coarsely ground wheat or barley	0	0	12	0	0
Cottonseed meal	2	2	1½	2	1¾
Silage	16	0	8	0	0
Cottonseed hulls	0	0	4	4	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	6	0	0	0
Ground grain sorghum fodder	0	0	0	0	6
Sixth Four Weeks					
Ear corn chops or grain sorghum head chops	0	15	0	15	0
Corn chops or sorghum grain chops	14	0	0	0	14
Coarsely ground wheat or barley	0	0	14	0	0
Cottonseed meal	2	2	1½	2	1¾
Silage	12	0	6	0	0
Cottonseed hulls	0	0	3	3	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	5	0	0	0
Ground grain sorghum fodder	0	0	0	0	5

4. Rations for 500- to 750-Pound Yearlings [83]

Each animal should receive 1/10 pound of calcium supplement per day, with any ration used. Five alternative rations are given on page 842.

Constituent of ration	Amount, pounds				
	No. 1	No. 2	No. 3	No. 4	No. 5
First Four Weeks					
Ear corn chops or grain sorghum head chops	0	4	0	4	0
Corn chops or sorghum grain chops	3	0	0	0	3
Coarsely ground wheat or barley	0	0	3	0	0
Cottonseed meal	2¼	2¼	2	2½	2
Silage	35	0	18	0	0
Cottonseed hulls	2	0	7	14	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	14	0	0	0
Ground grain sorghum fodder	0	0	0	0	14
Second Four Weeks					
Ear corn chops or grain sorghum head chops	0	7	0	7	0
Corn chops or sorghum grain chops	6	0	0	0	6
Coarsely ground wheat or barley	0	0	6	0	0
Cottonseed meal	2¼	2¼	2	2½	2
Silage	35	0	18	0	0
Cottonseed hulls	2	0	6	14	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	14	0	0	0
Ground grain sorghum fodder	0	0	0	0	14
Third Four Weeks					
Ear corn chops or grain sorghum head chops	0	10	0	10	0
Corn chops or sorghum grain chops	9	0	0	0	9
Coarsely ground wheat or barley	0	0	9	0	0
Cottonseed meal	2¼	2¼	1½	2½	2
Silage	30	0	16	0	0
Cottonseed hulls	2	0	6	12	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	12	0	0	0
Ground grain sorghum fodder	0	0	0	0	12
Fourth Four Weeks					
Ear corn chops or grain sorghum head chops	0	13	0	13	0
Corn chops or sorghum grain chops	12	0	0	0	12
Coarsely ground wheat or barley	0	0	12	0	0
Cottonseed meal	2¼	2¼	1½	2½	2
Silage	30	0	15	0	0
Cottonseed hulls	2	0	5	12	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	12	0	0	0
Ground grain sorghum fodder	0	0	0	0	12
Fifth Four Weeks					
Ear corn chops or grain sorghum head chops	0	16	0	16	0
Corn chops or sorghum grain chops	15	0	0	0	15
Coarsely ground wheat or barley	0	0	15	0	0
Cottonseed meal	2¼	2¼	1½	2½	2
Silage	25	0	14	0	0
Cottonseed hulls	2	0	5	10	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	10	0	0	0
Ground grain sorghum fodder	0	0	0	0	10

5. Rations for 800- to 1,000-Pound Cattle [83]

Each animal should receive 1/10 pound of a calcium supplement per day, with any ration used. Five alternative rations are given.

Constituent of ration	Amount, pounds				
	No. 1	No. 2	No. 3	No. 4	No. 5
First Four Weeks					
Ear corn chops or grain sorghum head chops	0	6	4	6	0
Corn chops or sorghum grain chops	6	0	0	0	6
Coarsely ground wheat or barley	0	0	4	0	0
Cottonseed meal	2½	2½	2½	3	2½
Silage	44	0	22	0	0
Cottonseed hulls	2	0	8	16	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	18	0	0	0
Ground grain sorghum fodder	0	0	0	0	16
Second Four Weeks					
Ear corn chops or grain sorghum head chops	0	9	5	9	0
Corn chops or sorghum grain chops	9	0	0	0	9
Coarsely ground wheat or barley	0	0	5	0	0
Cottonseed meal	2½	2½	2½	3	2½
Silage	40	0	20	0	0
Cottonseed hulls	2	0	8	16	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	16	0	0	0
Ground grain sorghum fodder	0	0	0	0	14
Third Four Weeks					
Ear corn chops or grain sorghum head chops	0	12	6	12	0
Corn chops or sorghum grain chops	12	0	0	0	12
Coarsely ground wheat or barley	0	0	6	0	0
Cottonseed meal	2½	2½	2½	3	2½
Silage	36	0	20	0	0
Cottonseed hulls	2	0	8	14	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	14	0	0	0
Ground grain sorghum fodder	0	0	0	0	12
Fourth Four Weeks					
Ear corn chops or grain sorghum head chops	0	15	7	15	0
Corn chops or sorghum grain chops	15	0	0	0	15
Coarsely ground wheat or barley	0	0	7	0	0
Cottonseed meal	2½	2½	2½	3	2½
Silage	32	0	18	0	0
Cottonseed hulls	2	0	8	12	0
Legume hay	0	0	0	2	1
Grass hay, sweet sorghum fodder or hay	0	12	0	0	0
Ground grain sorghum fodder	0	0	0	0	10

C. Feeding of Dairy Cattle

1. General

The value of protein in the daily ration has long been recognized, and has been the object of much experiment station research. Cottonseed meal is used in dairy rations quite extensively. In addition to supplying protein, cottonseed meal is a source of phosphorus and of fat in the ration.

Early work in North Carolina by Halverson and Sherwood [24] on the feeding of cottonseed meal with different roughages to lactating dairy cows indicated that cottonseed meal could be satisfactorily feed over extended periods, and showed conclusively the necessity of including roughage supplying adequate vitamin A in dairy rations. Huffman,[84] of Michigan, showed that cottonseed meal was a good source of protein for dairy cows and that dairy cows required good rations to furnish adequate vitamin A. Huffman and Moore [85] demonstrated that cottonseed meal was not a costly feed for dairy cows and, later, that liberal feeding of cottonseed meal to dairy cattle from 3 months to 4 years of age, along with good quality hay, had no apparent ill effect on health, reproduction, or lactation.

Long-time, comprehensive feeding of dairy cows on a ration of cottonseed meal and prairie hay by Kuhlman and co-workers,[86] at the Oklahoma Station, have proved conclusively that cottonseed meal may be used in dairy rations in as large amounts as are necessary to supply adequate amounts of protein, and even in much larger amounts if price makes it economical to do so, provided that it is fed with roughage or pasture supplying sufficient vitamin A.

These extensive experiments in North Carolina, Michigan, Oklahoma, and other states, as well as many other experiments, have conclusively demonstrated that many early ideas about cottonseed meal were erroneous. Many experiments conducted specifically for the purpose of answering questions arising from these erroneous ideas have proved, contrary to previous belief, that cottonseed meal neither causes nor aggravates such dairy problems as udder or reproduction troubles and constipation.

In studying the feeding of large quantities of cottonseed meal to lactating cows at the Texas Station, Copeland [87] found that its use as the sole concentrate did not produce udder or reproduction troubles, nor was it constipating. In New Mexico, Cunningham and Addington [88] concluded

[84] C. F. Huffman, *Michigan Agr. Expt. Sta. Quart. Bull.*, **11,** 4 (1929).
[85] C. F. Huffman and L. A. Moore, *J. Dairy Sci.*, **12,** 410–418 (1929).
[86] A. H. Kuhlman, E. Weaver, and W. D. Gallup, *Oklahoma Agr. Expt. Sta. Biennial Rept.*, p. 8 (1936).
[87] O. C. Copeland, *unpublished Thesis,* Texas A. & M. College, 1929; *Texas Agr. Expt. Sta. Bull.*, **451** (1932).
[88] O. C. Cunningham and L. H. Addington, *New Mexico Agr. Expt. Sta. Bull.*, **226** (1934).

from their work that cottonseed meal is a good source of protein for dairy animals. Hotis and Woodward,[89] at the Beltsville Station, studied the heavy feeding of cottonseed meal in relation to udder troubles and concluded that feeding of cottonseed meal did not aggravate udder troubles.

Reed and associates,[90] in Michigan, found that 2 pounds of cottonseed meal daily per head could be fed to dairy calves 5 months of age or older receiving all of the silage and good hay they would eat. Graves and Dawson,[91] in reporting recent work by U.S.D.A. Stations on the rates of growth of dairy heifers on different rations, state that 1 pound of cottonseed meal, fed with silage, proved superior to a ration of alfalfa hay, silage, and 2 pounds of grain.

In addition to cottonseed meal, the cotton crop furnishes a roughage that has proved to be valuable for dairy cattle. Lush and associates,[92] at the Louisiana Station, compared cottonseed hulls with grass hays for milk production, and found that, when fed in a balanced ration supplying adequate protein, calcium and some green feed, cottonseed hulls were superior to carpet- and Bermuda-grass hay, and almost equal to high-quality Bermuda hay, for milk production. Hollaman,[93] of North Carolina, found that a hull–molasses mixture was more economical for both milk and fat production than beet pulp.

Comparing cottonseed hulls with Bermuda, sudan, and sorghum hays for growing dairy heifers, Copeland,[94] of Texas, found that hulls can be used as the sole roughage when enough grain is fed to provide the amount of productive energy required for normal growth and the animals are allowed access to pasture during at least six months of each year. Use of cottonseed hulls as the sole dry roughage under these conditions did not impair breeding performance of the heifers.

Darnell[95] states that cottonseed meal may safely make up 33% of the grain ration. The calf meal mixture given in the table on page 846, according to Darnell, has given good results in the feeding of dairy calves. It may be made on the farm from the proper ingredients.

According to the recommendations of Darnell, this feed should be thoroughly mixed, 1 pound of the mixture added to 8 pounds of water, the whole warmed to proper feeding temperature, stirred well, and fed in the same manner as skim milk.

[89] R. P. Hotis and T. E. Woodward, *U.S. Dept. Agr. Tech. Bull.*, **473** (1935).
[90] O. E. Reed, C. F. Huffman, and L. H. Addington, *J. Dairy Sci.*, **11,** 488–507 (1928).
[91] R. R. Graves and J. R. Dawson, *U.S. Dept. Agr. Circ.*, **No. 560** (1940).
[92] R. H. Lush, C. H. Staples, J. L. Fletcher, and S. Stewart, *Louisiana Agr. Expt. Sta. Bull.*, **238** (1933).
[93] J. S. Hollaman, *unpublished Thesis,* North Carolina State College of Agr. and Eng., 1939.
[94] O. C. Copeland, *Texas Agr. Expt. Sta. Ann. Rept.*, p. 92 (1932).
[95] A. L. Darnell, *Texas A. & M. College Bull.*, **11,** No. 15, 9 (1940).

Constituent	Amount, pounds	Constituent	Amount, pounds
Skim milk powder	20	Alfalfa leaf meal	7
54% protein cottonseed meal	18	Red Dog flour	6
Soybean meal	15	Hominy feed	7
Linseed oil meal	15	Salt	1
Dried whey	10	Oyster shell powder	1

Lush and Neasham [96] state that for dairy cows cottonseed meal furnishes the most important and the cheapest source of protein and sometimes of the total feeding value of any concentrate. They further state that cold-pressed cottonseed cake can sometimes be used profitably for feeding dairy cattle on Bermuda, Johnson grass, or rice stubble pasture, and that 2 pounds of cold-pressed cake are equal to 1 pound of choice meal and ½ pound of corn in a grain ration.

Kuhlman and Gallup [97] reported results with three experiments—including a total of 32 cows—which gave information on the value of cottonseed meal when it is fed in excess of the amount required to meet the protein requirements of dairy cattle. The concentrate mixture fed in the check ration consisted of 400 pounds ground No. 2 corn, 200 pounds ground oats, 200 pounds wheat bran, 100 pounds cottonseed meal (43% protein), and 9 pounds salt. In the experimental ration, cottonseed meal replaced 44.5% of this concentrate mixture and constituted slightly more than 50% of the total concentrates fed. Alfalfa hay, U.S. No. 1, extra green, was fed as the sole roughage. When fed the check ration, the cows on the average produced 29.96 pounds of 4% fat-corrected milk daily, and consumed 41.6 pounds of the concentrate mixture and 68.4 pounds of alfalfa hay for each 100 pounds of 4% milk. On the experimental ration, the cows produced an average of 30.44 pounds of 4% milk daily, and consumed 22.5 pounds of the concentrate mixture plus 18 pounds of extra cottonseed meal or 40.5 pounds total concentrates and 67.4 pounds of alfalfa hay for each 100 pounds of 4% milk. Each 100 pounds of cottonseed meal substituted for the concentrate mixture were equivalent to 109.8 pounds of the concentrate mixture which it replaced. They concluded that, when the cost of cottonseed meal does not exceed the cost of corn, oats and bran, it may replace the latter with satisfactory results even when cottonseed meal constitutes one-half of the total concentrates fed with alfalfa hay.

In order for dairy cattle to utilize cottonseed meal or other single feeds efficiently, it has been shown by experiment and by observation that

[96] R. H. Lush and E. W. Neasham, *Louisiana Univ. Agr. Expt. Sta. Circ.*, **No. 18** (1937).

[97] A. H. Kuhlman and W. D. Gallup, *J. Animal Sci.*, **1**, 348 (1942).

critical attention must be given to pastures, minerals, and vitamins in the ration. Cottonseed hulls, comparable to average grass hay in value, can supply at least one-half the required roughage and are good to use together with grazing. Hulls are free of dirt and trash, and easy to feed with other roughage or to use for furnishing needed bulk in concentrate mixtures. The Educational Service of the National Cottonseed Products Association [83] reports that many mills make mixtures of cottonseed meal and hulls to feed with ground grains and hay. Some mixtures also contain molasses and a calcium supplement. Because mixtures vary, feeders should follow specific instructions for the mixture used. A widely used meal and hull mixture contains 80% hulls and 20% meal. Cows require about 5 pounds of this mixture and 2 pounds of ground grain for each gallon of milk produced, in addition to pasture or hay. If the mixtures contain no calcium, this mineral should be kept available, along with salt. To insure enough vitamin A, at least 6 pounds of green hay should be fed daily unless the cows are on good pasture.

Cows should have all of the roughage they will eat (about 2 pounds of dry roughage or 6 pounds of silage for 100 pounds of live weight). Feeding 3 pounds of silage and 1 pound of dry roughage daily for each 100 pounds of live weight gives good results. Wet beet pulp or roots may be substituted at the rate of 6 pounds for 1 pound of dry roughage.

2. Rations for Different Types of Roughages and Pasture

Concentrate mixtures, containing cottonseed meal, and recommended by the Educational Service of the National Cottonseed Products Association [83] (after checking with the results of research workers and dairymen in many of the agricultural colleges) are given here for different types of roughages and pasture.

(a) For Use with Low-Protein Roughages or for Cows on Poor Pasture. The mixtures given on p. 846, containing 18–20% of crude protein (figures in pounds), should be used with low-protein roughages, such as sorghum or corn silage; grain sorghum fodder; sweet sorghum fodder or hay; corn stover; cottonseed hulls; Sudan, Johnson, Bermuda, prairie and other grass hays; or poor, dry pasture of any type.

Jerseys or Guernseys should be fed 1 pound of any of the mixtures for each ½ pounds of milk, or 3½ pounds for each gallon of milk produced daily. Holsteins, Ayrshires, or Milking Shorthorns should be fed 1 pound of mixture for each 3 pounds of milk, or 2¾ pounds for each gallon of milk produced daily.

A simplified mixture which is practical under average farm conditions is 100 pounds of ground grain with 40 pounds of 41% protein cottonseed meal or 50 pounds of 36% meal. With such a mixture, calcium and salt should be kept available.

Number 1

Corn meal, ground barley or wheat, or sorghum grain chops	500
Cottonseed meal	300
Wheat bran	200
Ground oats	100
Ground limestone or oyster shell	22
Salt	11

Number 2

Hominy feed, corn meal, ground barley or wheat	100
Rice bran or wheat bran	100
Ground oats or barley	100
Cottonseed meal	100
Ground limestone or oyster shell	8
Salt	4

Number 3

Corn meal, sorghum grain chops, or ground wheat	200
Wheat bran or ground oats	100
Cottonseed meal	100
Ground limestone or oyster shell	8
Salt	4

Number 4

Corn meal, ground barley or wheat, or sorghum grain chops	600
Cottonseed meal	300
Cottonseed hulls	100
Ground limestone or oyster shell	20
Salt	10

Number 5

Ear corn chops (crushed snapped corn)	300
Cottonseed meal	200
Ground oats or wheat bran	200
Ground limestone or oyster shell	14
Salt	7

Number 6

Rolled barley, sorghum grain chops, or corn meal	300
Wheat bran	200
Dried citrus peel and pulp or dried beet pulp	200
Cottonseed meal	300
Ground limestone or oyster shell	20
Salt	10

Number 7

Ear corn chops or grain sorghum head chops	700
Cottonseed meal	300
Ground limestone or oyster shell	20
Salt	10

Number 8

Sweet potato meal (dehydrated)	300
Ground oats, wheat bran, or rice bran	200
Cottonseed meal	300
Ground limestone or oyster shell	16
Salt	8

Number 9

Whole pressed cottonseed	300
Wheat bran or ground oats	100
Corn meal, ground barley, or sorghum grain chops	200
Ground limestone or oyster shell	12
Salt	6

Number 10

Whole pressed cottonseed	400
Ground barley or wheat	300
Rice bran or wheat bran	100
Ground limestone or oyster shell	16
Salt	8

(b) For Use with Medium-Protein Roughages or for Cows on Fair Pasture. The mixtures given below (figures in pounds) contain approximately 15% of crude protein, and are satisfactory for use with a combination of low-protein and high-protein roughages, such as corn or sorghum silage and fodder with alfalfa or other legume hay; Johnson grass or other grass hays with legume hay; equal amounts of cottonseed hulls and legume hay; or fair pasture, such as Bermuda grass and other native grasses.

Jerseys or Guernseys should be fed 1 pound of mixture for each 3 pounds of milk, or 2¾ pounds for each gallon of milk produced daily. Holsteins, Milking Shorthorns or Ayrshires should be fed 1 pound of mixture for each 3½ pounds of milk, or 2½ pounds for each gallon of milk produced daily.

A simplified mixture is 100 pounds of ground grain with 25 pounds of cottonseed meal.

Number 11

Corn meal, ground wheat, or sorghum grain chops	400
Ground oats or barley	200
Cottonseed meal	100
Ground limestone or oyster shell	7
Salt	7

Number 12

Sweet potato meal (dehydrated)	400
Ground oats, wheat bran, or rice bran	200
Cottonseed meal	200
Ground limestone or oyster shell	8
Salt	8

Number 13

Corn meal, ground wheat, or sorghum grain chops	700
Cottonseed meal	200
Cottonseed hulls	100
Ground limestone or oyster shell	10
Salt	10

Number 14

Ear corn chops or grain sorghum head chops	400
Cottonseed meal	100
Ground limestone or oyster shell	5
Salt	5

Number 15

Corn meal, ground wheat, or sorghum grain chops	400
Ground oats or barley	200
Wheat bran or rice bran	100
Cottonseed meal	100
Ground limestone or oyster shell	8
Salt	8

Number 16

Ground wheat, corn meal, or sorghum grain chops	200
Ground oats or barley	200
Dried citrus peel and pulp or dried beet pulp	150
Cottonseed meal	100
Ground limestone or oyster shell	6½
Salt	6½

Number 17

Ear corn chops (crushed snapped corn)	300
Ground oats or wheat bran	200
Cottonseed meal	100
Ground limestone or oyster shell	6
Salt	6

Number 18

Rolled barley or wheat	300
Ground oats	100
Dried citrus peel and pulp or dried beet pulp	100
Wheat bran	100
Cottonseed meal	100
Ground limestone or oyster shell	7
Salt	7

Number 19

Whole pressed cottonseed	200
Ground oats or wheat bran	200
Corn meal, ground barley, or sorghum grain chops	400
Ground limestone or oyster shell	8
Salt	8

Number 20

Whole pressed cottonseed	200
Ground wheat, corn meal or ground barley	300
Dried citrus peel and pulp or dried beet pulp	200
Ground limestone or oyster shell	7
Salt	7

(c) For Use with High-Protein Roughages or for Cows on Good Green Pasture. The following mixtures (figures in pounds) contain approximately 12% crude protein and are for use with high-protein roughages, such as alfalfa, lespedeza, pea vine, soybean, kudzu, peanut, mung bean and other legume hays—or for cows on good pasture which provides ample grazing. Cows that give 2 gallons of milk daily or less usually require no grain mixture if on good pasture or receiving ample legume hay, but higher producing cows should receive one of these mixtures.

Jerseys and Guernseys should be fed 1 pound of mixture for each 3½ pounds of milk, or 2½ pounds for each gallon of milk produced daily. Holsteins, Ayrshires, or Milking Shorthorns should be fed 1 pound of mixture for each 4 pounds of milk, or 2 pounds for each gallon of milk produced daily.

A simplified mixture is 100 pounds of ground grain and 10 pounds of cottonseed meal.

Number 21

Corn meal or sorghum grain chops	600
Wheat bran or ground oats	200
Cottonseed meal	25
Salt	8

Number 22

Ear corn chops or grain sorghum head chops	500
Ground wheat or barley	200
Cottonseed meal	50
Salt	7½

Number 23

Sweet potato meal (dehydrated)	300
Ground oats, wheat bran or rice bran	100
Cottonseed meal	100
Salt	5

Number 24

Sorghum grain chops or corn meal	300
Ground wheat or barley	300
Cottonseed meal	50
Cottonseed hulls	100
Salt	7½

Number 25

Ear corn chops or grain sorghum head chops	900
Cottonseed meal	100
Salt	10

Number 26

Rolled barley or wheat	300
Corn meal or sorghum grain chops	300
Dried citrus peel and pulp or dried beet pulp	300
Cottonseed meal	100
Salt	10

Number 27

Whole pressed cottonseed	100
Corn meal or sorghum grain chops	600
Ground oats or barley	300
Salt	10

Number 28

Whole pressed cottonseed	100
Dried citrus peel and pulp or dried beet pulp	200
Ground barley or wheat	200
Sorghum grain chops or corn meal	200
Salt	7

D. Feeding of Sheep

1. General

Cottonseed cake and meal are standard protein supplements for the feeding of sheep, being extensively used for winter maintenance of range and farm flocks, and in the feedlot fattening rations. Feeding trials with cottonseed products for sheep have dealt largely with the study of fattening rations for lambs.

King and Harper,[98] of the Indiana Station, reported an increase in the rate of gain, reduced cost of gain, and increased market value of lambs when cottonseed meal supplemented a ration of clover hay, corn grain, and corn silage. Maynard and Osland,[99] in Colorado, found that 1 ton of cottonseed meal replaced 1,700 pounds of barley and almost 2 tons of alfalfa hay in the fattening ration of lambs fed four months. Maynard and associates,[100] in tests at the Utah Station, found that the addition of cottonseed meal to a barley and alfalfa ration increased the rate of gain and finish of lambs. In recent Colorado tests by Morton and associates,[101]

[98] F. G. King and C. Harper, *Purdue Agr. Sta. Bull.*, **360** (1932).

[99] E. J. Maynard and H. B. Osland, *Colorado Agr. Expt. Sta. Press Bull.*, **68** (1929).

[100] E. J. Maynard, A. C. Esplin, and S. R. Boswell, *Utah Agr. Expt. Sta. Bull.*, **238** (1932).

[101] G. E. Morton, H. B. Osland, and R. C. Tom, *Colorado Agr. Expt. Sta. Press Bull.*, **91** (1937).

1 ton of cottonseed cake fed to fattening lambs receiving corn and alfalfa hay replaced 3,300 pounds of corn and 140 pounds of alfalfa hay.

Neale,[102] at the New Mexico Station, has studied the feeding of varying amounts of cottonseed meal in different rations for fattening lambs. He concluded that cottonseed meal may be fed as the sole concentrate to lambs receiving good quality roughage, and that as much as 1 pound of meal may be fed satisfactorily, with cottonseed hulls as the only roughage, for 60 days. He also found that lambs should receive at least 0.35 pound of cottonseed meal daily per head when hegari fodder is the only roughage, and that cottonseed meal may have a greater effect in increasing the efficient use of roughage than it does on the efficient use of grain.

Feeding trials by Mackey and Jones,[103] at the Texas Station, show that cottonseed cake in rations with either threshed milo or oats and alfalfa produced greater gains and effected a considerable saving in both grain and alfalfa. These workers stated that lambs receiving cottonseed cake were always more eager for their concentrates, and it was possible to increase the amount of concentrates fed more rapidly in the lots where cake was fed also.

Schedule for Starting Lambs on Feed — Hand Feeding[a]

Number of days		Cottonseed cake (pea-size) per 100 lambs, lb.	Grain (shelled or threshed) per 100 lambs, lb.	Cottonseed cake (pea-size) per lamb, lb.	Grain (shelled) per lamb, lb.	Total concentrates per lamb lb.
1st[b]: Rest and fill on hay						
2nd:	P.M.	5	5	0.05	0.05	0.10
3rd:	A.M.	5	5	—	—	—
	P.M.	10	5	0.15	0.10	0.25
4th and 5th:	A.M.	10	10	—	—	—
	P.M.	10	10	0.20	0.20	0.40
6th and 7th:	A.M.	10	10	—	—	—
	P.M.	15	10	0.25	0.20	0.45
8th and 9th:	A.M.	10	10	—	—	—
	P.M.	15	15	0.25	0.25	0.50
10th and 11th:	A.M.	15	10	—	—	—
	P.M.	15	15	0.30	0.25	0.55
12th and 13th:	A.M.	16½	15	—	—	—
	P.M.	16½	15	0.33	0.30	0.63

[a] W. R. Nisbet and J. H. Jones, *Texas A. & M. Ext. Serv. Bull.*, **129** (1943).
[b] Rest period may be 1 to 7 days.

When hand feeding whole grains and pea-size cottonseed cake or screenings with carbonaceous roughages, the schedule shown in the above table may be used as a guide for feeding the concentrates, according to Nisbet and Jones.[104] Roughage is to be fed to the fullest extent.

[102] P. E. Neale, *New Mexico Agr. Expt. Sta. Bull.*, **200** (1932), and **272** (1940).
[103] A. K. Mackey and J. M. Jones, *Texas Agr. Expt. Sta. Bull.*, **465** (1932).
[104] W. R. Nisbet and J. H. Jones, *Texas A. & M. Ext. Serv. Bull.*, **129** (1943).

At the end of two weeks, the lambs will be eating ⅓ pound daily of cottonseed cake; this constitutes the full allowance which remains constant throughout the remainder of the feeding period. Since the hay is fed *ad lib.*, the only further adjustments in the ration will involve the grain. For most lots of lambs, the ration given for the twelfth and thirteenth day should be continued without change for one or two weeks to further develop feed capacity. Increases in grain may then be made according to the feeder's judgment; these increases should not exceed 5 pounds of grain per 100 lambs or 0.05 pound per lamb per day. By following this system, the lambs can be made to consume ⅔ pound of grain at 30 days, 1 pound at 40 days, and 1½ pounds at 50 days, and further increase may carry them up to and beyond 1¾ pounds per day.

If alfalfa hay furnishes the roughage, the cottonseed cake or meal may be reduced one-half.

If ground sorghum heads or ground ear corn are used, 25% more than shelled grains should be fed. In this case, cottonseed meal should be used and mixed thoroughly with the other ground feeds.

2. Feeding Method for Mixtures of Ground Feeds

Whole ground mixed rations may consist of bundle feeds, hays, cottonseed hulls, various grains, and cottonseed meal. The principle of feeding is the same as previously stated, but cottonseed meal is fed instead of pea-sized cottonseed cake. Table 207 may be taken as a guide.

TABLE 207

Schedule for Starting Lambs on Feed — Using Mixtures of Ground Feeds after All Preliminary Handling Has Been Done

Time	Grains, %	Cottonseed meal, %	Roughage, %
1st three days	10	5	75
2nd three days	15	7½	75½
2nd week	20	10	70
3rd week	25	12½	62½
4th week	30	12½	57½
5th week	35	12½	52½
6th week	40	12½	47½
7th week	45	12½	42½
8th week	50	12½	37½

The bundle feeds should be of good quality and free of mold and dirt. Grinding should be fine enough to crack most of the grains. Average grain sorghum bundles contain slightly too much grain (20–28%) for initial fill. If hay is available, it should be fed with the ground bundles and cottonseed meal mixture for about 10 days. If hay is not available, the mixture should be hand fed twice per day until lambs can take the whole ground bundle.

According to Nisbet and Jones,[104] cottonseed hulls as a roughage for lambs are used to better advantage when fed with an equal amount of alfalfa or other good hays. Mixed with cottonseed meal and ground grain, the hulls give ideal bulk to the ration and are especially valuable at the very start of the feeding period to give good fill.

3. Rations for Other Sheep and Goats

According to Ward and Wilson [83] of the Educational Service of the National Cottonseed Products Association, the following schedules for feeding cottonseed meal or cake and hulls to different classes of sheep and goats give good results.

(a) Sheep. For maintenance on average dry native grass or other low-protein roughage, dry ewes and wethers should be fed ¼ pound daily per head of cottonseed cake or other protein concentrates; bred ewes nursing lambs should be fed ⅖ to ½ pound daily per head. If poor feed conditions exist, the feeding of supplements is recommended at breeding time and a month afterward. If ample green feed is available or legume hay is fed, sheep usually get enough protein.

If grazing is short, roughage is needed in addition to the Cottonseed cake or meal. Good results are obtained from feeding 3 pounds of silage and ¼ pound of cottonseed meal daily per head, in troughs, to ewes before and after lambing, and also at breeding time and a month afterward. On range infested with bitterweed, the feeding of silage and cottonseed meal to sheep from December 15 to March 15 will help overcome trouble caused by bitterweed. Two to three pounds daily of a mixture of 20% cottonseed meal, 20% ground alfalfa or peanut hay, and 60% cottonseed hulls gives good results also. Bone meal, defluorinated phosphate, or other phosphorus supplement will prove beneficial on most ranges. Salt and fresh water should be available.

Lambs wintering on the range should start on ⅛ pound of cottonseed cake at weaning, with the amount increased to ¼ pound as winter advances. Sheep-size cake, cubes, or pellets may be fed on the ground, or pea-size cake in troughs.

In feeding whole pressed cottonseed, ewes require at least ½ pound daily, and lambs ⅓ pound daily per head.

(b) Angora Goats. Feeding a protein concentrate to angora goats increases the value of range grass and browse, and insures better kid crops and mohair yields.

How feeding should be started will depend on the condition of the range. When protein is scarce, does may be carried on ⅛ to ⅕ pound of cottonseed cake. Increased amounts of cake should be fed, beginning about January 1, on ranges infested with bitterweed or other noxious

plants, where goats start aborting 2 to 4 weeks prior to kidding, or where drouth is severe.

4. Feeding the Farm Flock

Well-planned sheep production is practical and profitable on many diversified farms, where sheep provide added income and are valuable to keep pastures free of weeds and to clean fields.

Ewes, suckling lambs, and even feeder lambs may be carried on small grain pastures during the late fall, winter, and spring. When the breeding flock comes off wheat or oat pasture and has no other grazing, roughage should be fed along with ¼ to ⅓ pound of cottonseed cake or meal daily per head, until permanent pastures supply ample feed. Sudan grass or other temporary pasture is ideal to supplement permanent pasture during the spring and summer.

Breeding ewes, to lamb from November to January, has several advantages: cold weather reduces parasites, winter and spring pastures provide grazing, and lambs are ready to sell on favorable spring markets.

If pastures are good, ewes bred for fall or spring lambing require no concentrate. If the pasture is short, ewes should have about 2 or 3 pounds of legume hay and ½ pound of grain per day; if the hay is nonlegume, they will need ¼ pound of cottonseed meal or cake and ½ pound of grain for 30 to 50 days before lambing. Ewes can get along on good pasture, but lambs will do much better if fed any available grain before weaning. Creep-feeding usually is desirable if lambs are to be marketed before the middle of June.

A mineral mixture of equal parts of bone meal, ground limestone, and salt should be available, with granulated salt *ad lib.*, in a sheltered trough. Fresh water should be provided at all times.

5. Creep-Feeding

Creep-feeding is desirable during dry seasons when green feed is short. Use of the creep should begin when lambs are 2 to 3 weeks old and the grain or other concentrates should be placed in the troughs regularly, once each day. Ample trough space must be provided. Troughs should be swept clean daily before grain is added. The amount of grain must be limited to what they will clean up daily. The addition of good legume hay in the creep will encourage the lambs to eat.

Any farm grains, such as shelled corn, sorghum grain, oats, or rolled barley, are satisfactory when lambs get ample milk. When the ewe's milk decreases, a good mixture is: 700 pounds of shelled corn, sorghum grain, rolled barley, or oats, or a mixture of any of these; and 100 pounds of pea- or pebble-size cottonseed cake, cubes, or pellets. Good hay should be available in racks with grain in the creeps.

6. Fattening for Market

The practice of buying lambs in the fall and placing them in fields to garner grain and forage that otherwise would be wasted is popular and sound. These lambs need ¼ to ⅓ pound of protein concentrate daily per head, and a salt and calcium supplement. Fresh water, readily accessible in clean troughs, is essential. Lambs will easily go on feed after fields are cleaned.

Lambs that go directly to the feed lot require special care to start them to feed. Lighter, weaker lambs should be fed separately. Regular feeding times and 12 linear inches of trough space per lamb aid efficient feeding. Unless legume hay is fed, lambs need $\frac{4}{10}$ ounce of limestone or oyster shell flour daily per head. Salt is always needed. Oats are ideal to start lambs on feed, but give best results if corn or other grain is gradually added until it makes up one-half of the grain ration.

In starting on feed, lambs should have ample rest, fresh water, and time to fill on sweet sorghum fodder, grass hay, or a mixture of 93% cottonseed hulls and 7% meal. In getting on full feed, lambs need all the hulls, sweet sorghum fodder, or grass hay they will eat, but any change to silage or legume hay should be gradual. Lambs started on meal and hulls may receive the full ration of cake or meal; those fed hay or fodder should start on $\frac{1}{10}$ pound of meal or cake, with the amount being gradually increased. Grain should be added gradually at the rate of $\frac{1}{20}$ pound daily per head, until the full amount is reached. In addition to roughage, lambs on full feed will eat 1 to 1½ pounds of grain and meal. Definite amounts of the concentrate mixture should be fed twice daily, before feeding roughage.

Suitable daily rations, for finishing 50- to 60-pound lambs are given below (figures in pounds).

Number 1	
Ear corn chops or milo head chops	1⅓
Cottonseed meal or cake	½
Sweet sorghum fodder or hay	½
Cottonseed hulls	½
Ground limestone or oyster shell flour	$\frac{4}{10}$ oz.

Number 2	
Corn, barley or milo	1
Cottonseed cake	⅓
Prairie hay	1½
Ground limestone or oyster shell flour	$\frac{4}{10}$ oz.

Number 3	
Rolled barley or wheat	½
Sorghum grain or dried beet pulp	½
Legume hay	2–3

Number 4	
Sorghum grain, barley, or wheat	1
Cottonseed meal	⅓
Ground grain sorghum fodder	1½
Ground limestone or oyster shell flour	$\frac{4}{10}$ oz.

Number 5	
Shelled corn, barley, or wheat	1
Cottonseed meal	⅓
Corn or sorghum silage	1½
Legume hay	1

Number 6	
Corn or sorghum grain	½
Wheat or barley	½
Wet beet pulp	2½–3
Alfalfa hay (chopped)	1½–2

When wheat or other winter pasture is good and lambs graze long enough, a desirable market finish can be produced without other feeds. Salt and a calcium supplement should be available.

7. "Lambing-Down" Crops

"Lambing-down" mature grain sorghums and other crops saves labor and often is practical; but care must be taken to prevent deaths from overeating. Range lambs need rest and treatment for internal parasites before being turned into fields; a good plan is to graze them on native grass, or feed hay or sorghum fodder with little or no grain for a few days.

To prevent overeating, enough of the field of mature grain should be harvested to furnish grazing the first 3 weeks. Lambs require about 150 pounds of grain per head for 100 days of feeding; and the yield of the harvested portion indicates the number of lambs the field can carry. Throughout the grazing period, lambs need ¾ pound of alfalfa hay daily per head, or ¼ pound of cottonseed meal with all the roughage they will eat.

Ample fresh water should be provided in a shallow trough, equipped with a float and drained or scrubbed two or three times weekly. Each lot of 250 lambs requires a water trough 12 feet long. A mineral mixture of equal parts of salt and ground limestone should be available.

E. Feeding of Swine

Because of the importance of an economical source of protein in swine rations for economical pork production, many experiment stations have studied the feeding of a high-protein feed or combination of protein feeds necessary to supplement carbohydrate grains and their by-products. Cottonseed meal as a protein supplement for swine has received considerable attention from scientific workers.

Extensive investigations on the feeding of cottonseed meal to swine have been conducted at the Texas Station.[48] These studies have proved cottonseed meal to be an efficient and economical source of protein in rations for brood sows, growing pigs, fattening hogs, and suckling pigs, provided that the meal is limited to 9% or less of the total ration. It has been found that a mixture of one-half cottonseed meal and one-half tankage, fed *ad lib.* as a protein supplement, gives better results than tankage, alone, for fattening pigs.

In Nebraska, Snyder[105] also found that various combinations of cottonseed meal and tankage stimulated the rate of gain over that with tankage, alone; and Maynard and co-workers,[106] at the Colorado Station.

[105] W. P. Snyder, *Nebraska Agr. Expt. Sta. Bull.*, **243** (1930).

[106] E. J. Maynard, H. B. Osland, and J. F. Brandon, *Colorado Agr. Expt. Sta. Bull.*, **396** (1932).

found that a mixture of equal parts of cottonseed meal and tankage proved efficient in the fattening ration.

Numerous investigations have been conducted on the value of cottonseed meal in fattening rations for producing firm pork. Hostetler and Halverson,[107] of North Carolina, fed rations productive of soft pork until the pigs reached 100 pounds in weight. From then until the pigs were finished for market, they were fed on a ration of corn, tankage, and cottonseed meal, with cottonseed meal making up 13% of the ration. Of the chilled carcasses, 97% graded firm. Other work by these authors indicated that adding cottonseed meal to the corn ration raises the melting point of the fat of pigs; and they conclude that for optimum results from 13 to 18% of the hardening ration for fattening pigs should be cottonseed meal. Hostetler and Foster [108] compared a protein supplement mixture of equal parts of cottonseed meal and fish meal with other combinations fed to the animals on pasture and found that it proved more efficient and more economical than any of the other combinations.

The Nebraska Station [109] found from numerous tests that combinations of cottonseed meal and tankage are superior to straight tankage for balancing a corn ration. These combinations proved more desirable under in dry-lot feeding than on pasture. A mixture of equal parts of cottonseed meal and tankage has proved as satisfactory as any combination used in the Nebraska tests. Cottonseed meal is very palatable to pigs, and in every case where cottonseed meal has been fed at the Nebraska Station, it is reported that there has been a considerable increase in feed consumption.

The United States Department of Agriculture [110] recommends that the most economical way to feed cottonseed meal to hogs is to mix it with tankage or other protein supplements, including alfalfa meal.

The Texas Extension Service [111] reports that where cottonseed meal is properly fed, it gives excellent results, and the cost of protein supplements can usually be reduced by its use. For best results, hogs fed rations containing cottonseed meal or other vegetable protein feeds should also have access to a good mineral mixture. A simple mixture of 40 pounds of bone meal, 40 pounds of ground limestone or oyster shell flour, and 20 pounds of salt is a good mineral mixture for swine.

Workers at the Indiana Station,[112] in a study of mixed supplements for hogs, found that when soybean oil meal was substituted for cottonseed

[107] E. H. Hostetler and J. O. Halverson, *North Carolina Agr. Expt. Sta. Tech. Bull.*, **61** (1939).

[108] J. E. Foster and E. H. Hostetler, *North Carolina Agr. Expt. Sta. Tech. Bull.*, **56** (1938).

[109] W. J. Loeffel, *Nebraska Expt. Sta. Circ.*, **No. 40** (1932).

[110] E. W. Sheets and E. H. Thompson, *U.S. Dept. Agr. Bull.*, **1179** (1930).

[111] E. M. Regenbrecht, *Texas Ext. Bull.*, **98** (1940).

[112] C. M. Vestal, *Indiana Agr. Expt. Sta. Bull.*, **508** (1945).

meal in their best protein mixture the rate of gain was reduced, and there were increases in the feed required to produce the gain, the daily consumption of the supplement, and the cost of gain. The Indiana Station experiments showed also that a supplement composed of 20 pounds of meat and bone scraps, 20 pounds of fish meal, 40 pounds of soybean meal, 10 pounds of cottonseed meal, and 10 pounds of linseed meal was more effective than simpler supplements in promoting rapid gains of hogs fed on pasture.

The results of feeding protein supplements with and without cottonseed meal are shown in detail in Table 208. It will be seen from these results that cottonseed meal improved the protein supplement materially.

TABLE 208

Effect of Different Protein Supplements for Hogs Fed on Pasture[a]

Supplement, parts by weight	Year	Average final weight of hogs, lb.	Average daily gain, lb.	Feed for 100 pounds of gain, lb.				Average daily supplement per hog, lb.	Feed cost per 100-lb. gain, dollars
				Corn	Supplement	Minerals	*Total*		
Supplement 5									
Meat and bone scraps 20	1938	227	1.70	318	40	0.6	359	0.68	3.73
Fish meal 20	1938[b]	236	1.68	351	34	1.7	387	0.57	3.90
Soybean oil meal 40	1939	225	1.72	310	37	0.8	348	0.65	3.35
Cottonseed meal 10									
Alfalfa leaf meal 10									
Average		229	1.70	326	37	1.0	364	0.63	3.66
Supplement 6									
Meat and bone scraps 20	1938	225	1.68	319	40	0.7	360	0.68	3.74
Fish meal 20	1938[b]	208	1.41	356	44	2.2	402	0.62	4.16
Soybean oil meal 50	1939	217	1.64	310	43	1.0	354	0.69	3.46
Alfalfa leaf meal 10									
Average		218	1.58	326	42	1.2	370	0.66	3.79

[a] C. M. Vestal, *Ind. Agr. Expt. Sta. Bull.*, **508** (1945).
[b] Winter of 1938–39. Other experiments were conducted in the summer.

As a feed for hogs, cottonseed meal is richer in certain minor nutritional factors than are some of the other vegetable protein feeds.[113] For example, cottonseed meal contains 2⅓ times as much vitamin B_1, 2⅙ times as much riboflavin, 1⅙ times as much niacin, and as much pantothenic acid as does soybean meal. Cottonseed meal also contains more phosphorus than do other vegetable protein feeds, such as soybean, linseed, and peanut meals.

[113] E. H. Hughes, E. W. Crampton, N. R. Ellis, and W. J. Loeffel, "Recommended Nutrient Allowance for Swine," *Natl. Research Council*, **No. 11**, 1944.

The Florida Station [114] recommends cottonseed meal in the amount of ½ of the supplement, the other half to consist of tankage or fish meal.

Smith [115] reports that experiments at many stations have shown that a combination of cottonseed meal and tankage gives good results with swine. In nine of twenty-two feeding trials which Smith summarized, no appreciable difference was noted between the use of tankage and cottonseed meal, and tankage and linseed or soybean oil meal.

Robinson [37] has summarized the results of twenty experiments in which cottonseed meal was substituted for linseed meal in trio-mixtures for pigs, either in the dry lot or on pasture.

Smith [115] gives the following rations containing cottonseed meal for swine feeding:

A. For growing and fattening pigs in dry lot or on forage.
   1. A feed mixture, hand-fed or self-fed, composed of about 84% ground corn or other grain plus 10 to 12% of a trio-mixture composed of equal parts by weight of cottonseed meal, tankage, and alfalfa meal (or 2 parts cottonseed meal, 1 part tankage, and 1 part alfalfa meal) plus 1½% of a good mineral mixture, such as 2 parts ground limestone, 2 parts special steam bone meal, and 1 part common salt. When forage or other green feed is available, the alfalfa meal should be eliminated.
   2. Corn or other grain, self-fed, plus a mixture of 2 parts cottonseed and 1 part tankage or fish meal (or equal parts tankage and fish meal), self-fed, plus fine alfalfa or other legume hay in a rack, plus a good mineral mixture, self-fed.

B. For brood sows during the gestation period.
   1. Ration number 1 above, fed by hand in such amounts as will maintain the desirable condition and weight in the sows.

C. For sows suckling pigs.
   1. A feed mixture, hand-fed, composed of 80% ground corn or other grain, 9% cottonseed meal, 4% tankage or other equivalent supplement, plus 5% alfalfa meal, and 2% of a mineral mixture.

The cottonseed meal studies at the Texas Station [48] showed that it is possible to feed cottonseed meal safely to all classes of hogs when certain amounts and balanced rations are used. The Texas work was divided into eight experiments, which included studies of the following: (*a*) cottonseed meal in rations for brood-sows, boars, and for suckling pigs; (*b*) the use of minerals in cottonseed meal rations for pigs; (*c*) the feeding of raw cottonseed to fattening pigs; (*d*) feeding cottonseed meal, *ad lib.*, in self feeders; (*e*) the feeding of varying amounts of cottonseed meal to find the optimum amount that can be used in swine rations; and (*f*) the feeding of

[114] A. L. Shealy and W. J. Sheely, *Florida Agr. Expt. Sta. Bull.*, **236** (1931).
[115] W. W. Smith, *Pork Production.* Macmillan, New York, 1937.

a half and half cottonseed meal–tankage mixture, *versus* tankage alone as a protein supplement for fattening hogs.

The Texas experiments indicate that a ration containing not over 9% cottonseed meal can be fed to fattening hogs and to breeding hogs with good results. Three sows, fed a cottonseed meal ration, in three years farrowed 17 litters of pigs that averaged 9.49 pigs per litter. The litters farrowed from the tankage-fed sows during the same period averaged 10.82 pigs per litter. The average birth weight of the pigs from the cottonseed-meal-fed sows was 2.75 pounds. The pigs from the tankage-fed sows averaged 2.74 pounds at birth. Two gilts out of the cottonseed-meal-fed sows were fed continuously on the same ration and farrowed three consecutive litters each of second generation cottonseed-meal-fed pigs that averaged 10.5 pigs per litter.

The pigs receiving a ration containing 9% cottonseed meal gained on the average 0.23 pounds daily per pig less than did the pigs on a straight tankage ration; and 36 pounds of cottonseed meal replaced 23 pounds of

TABLE 209

Protein Supplement Mixtures to Use with Grain[a]

Constituent	For hogs in dry lot, pounds		For hogs on pasture, pounds	
	Supplement A (40%)	Supplement B (40%)	Supplement C (40%)	Supplement D (40%)
Cottonseed meal	50	30	50	30
Peanut, soybean or linseed meal	0	30	0	30
Meat scraps, fish meal, or tankage	30	20	30	20
Ground choice legume hay	20	20	0	0
Wheat gray shorts or ground wheat	0	0	20	20

Note: Ground oats can replace 10 pounds of wheat gray shorts or ground wheat in Supplements C and D. If animal protein cannot be obtained, a mixture of 100 pounds of cottonseed meal, 100 pounds of peanut, soybean or other protein meal, 10 pounds of ground limestone, and 2 pounds of salt can replace Supplements A, B, C, or D. When used to replace Supplements A and B, provide legume hay in racks. Protein supplements may be hand-fed or self-fed, *ad lib.*, with grain. When mixed with ground grain, they may be self-fed or hand-fed in a dry mixture or in a swill made up at feeding time.

[a] A. L. Ward and R. W. Wilson, National Cottonseed Products Association, *Feeding Practices*, 1946.

tankage and 6 pounds of grain for each 100 pounds of gain. A mixture of limestone and salt was shown to be necessary in cottonseed meal rations for pigs.

Raw cottonseed did not prove to be satisfactory as a feed for hogs. The pigs that were fed raw cottonseed scoured badly, and died. The pigs getting one-half cottonseed meal and one-half tankage mixture, fed in self-feeders, *ad lib.*, with milo chops, gained on the average 0.095 pound

more daily per pig than did the pigs that received only the tankage and milo chops.

The National Cottonseed Products Association [83] has computed rations containing cottonseed meal for hogs from experimental data obtained at the experiment stations in the United States. Some of these rations are presented in tabular form below.

Table 209 lists protein supplement mixtures. Table 210 shows the amounts of these supplements to combine with grains in balanced rations. For example, to feed corn meal and a protein supplement to pigs weighing up to 75 pounds, the first line of Table 210 shows that it takes 30 pounds

TABLE 210

Amounts of Protein Supplement Needed with Grain for Fattening and Breeding Hogs[a]

Type of hog	Percentage of protein needed in ration	Supplement to use (Table 209)	Pounds of supplement required in each 100 pounds of feed mixture			
			With corn meal	With sorghum grain chops	With ground barley	With ground wheat
In Dry Lot						
Pigs up to 75 pounds	18	A	30	25	22	20
Growing pigs, 75–150 pounds	16	A	24	18	16	14
Fattening hogs, 150–250 pounds	14	B	16	12	8	6
Bred sows	14	A	16	12	8	6
Nursing sows	16	A	24	18	16	14
On Pasture						
Pigs up to 75 pounds	18	C	30	25	22	20
Growing pigs, 75–150 pounds	14	C	16	12	8	6
Fattening hogs, 150–250 pounds	12	D	10	8	6	6
Bred sows	12	C	10	8	6	6
Nursing sows	14	C	16	12	8	6

[a] A. L. Ward and R. W. Wilson, National Cottonseed Products Association, *Feeding Practices*, 1946.

of Supplement A, in Table 209, in a 100-pound mixture. Therefore, 70 pounds of corn meal and 30 pounds of Supplement A should be used.

Wheat and barley will supply 12% protein, but in order to insure the quality of protein, a minimum of 6 pounds of a protein supplement is recommended. Rice bran or polishings can replace up to one-half the grain. A mineral mixture should be available, *ad lib.*

Four mixtures that are suitable for sows are shown on the next page.

Constituent of ration	Amount, pounds			
	No. 1	No. 2	No. 3	No. 4
Corn meal or sorghum grain chops	65	50	60	0
Coarsely ground wheat or finely ground barley	0	40	0	74
Ground oats	0	0	15	20
Wheat gray shorts, rice bran or polishings	0	0	15	0
Cottonseed meal, peanut meal, or soybean meal	7	7	6	4
Meat scraps, fish meal, or tankage	3	3	4	2
Limestone, oyster shell flour, or wood ashes	1½	1½	1½	1½
Salt	½	½	½	½

Pigs start eating when about 3 weeks old. Creep-feeding gives good results with the mixtures given below, with those for pigs in Table 210, or with grain and a protein supplement in separate compartments of a self-feeder. If good pasture is not available, 10 pounds of grain should be replaced with 10 pounds of ground legume hay.

Four mixtures for growing pigs are given below.

Constituent of ration	Amount, pounds			
	No. 1	No. 2	No. 3	No. 4
Corn meal or sorghum grain chops	55	40	0	70
Coarsely ground wheat or finely ground barley	0	45	68	15
Ground oats	20	0	20	0
Wheat gray shorts or rice polishings	10	0	0	0
Cottonseed meal, peanut meal, or soybean meal	9	10	8	10
Meat scraps, fish meal, or tankage	6	5	4	5
Limestone, oyster shell flour, or wood ashes	1½	1½	1½	1½
Salt	½	½	½	½

F. Feeding of Horses and Mules

Cottonseed meal and hulls are extensively used in rations of horses and mules throughout the Cotton Belt.

Curtis,[116] of the North Carolina Station, in reporting the results of a three-year test in the feeding of cottonseed meal to draft animals stated:

"There has been considerable diversity of opinion regarding the use of cottonseed meal for draft animals. On the whole, however, the weight of evidence seems to be in favor of this feed for work stock when it is fed with judgment. When fed in quantities ranging from 10–15% of the total ration by weight, it will generally be eaten satisfactorily without any observable detrimental results. Cottonseed meal is an excellent laxative and for this reason, it is desirable to feed with corn,

[116] R. S. Curtis, *North Carolina Agr. Expt. Sta. Bull.*, **215** and **216** (1911).

aside from the fact that it furnishes the deficiency of protein in corn. The effect of the meal on the coat of the animal is to make it smooth and glossy, having the same effect in this respect as linseed meal."

At the Iowa Station,[117] 6 pounds of cottonseed meal was as effective as eight pounds of linseed oil meal in balancing 100 pounds of a grain mixture containing 15 pounds of ground oats, the balance consisting of ground corn. The horses receiving cottonseed meal consumed 1.07 pounds per head daily. This report concluded that the health, spirit, and endurance of work horses were the same when fed corn with a moderate amount of oil meal, gluten feed, or cottonseed meal, as when fed a corn and oats ration supplying a similar nutritive ratio. In the Iowa test, cottonseed meal gave somewhat better results on the whole than linseed meal. The ration containing cottonseed meal was fully as palatable and as efficient in maintaining the health and weight of the horses, was less laxative in effect, and was a little cheaper. At the usual prices of the feeds, the use of cottonseed meal resulted in a substantial lowering of the cost of maintaining the horses.

Bell and Williams,[118] of the Bureau of Animal Industry, in a report covering the feeding of cottonseed meal to horses, stated that 1 pound a day per 100 pounds live weight is the most satisfactory quantity to feed.

Williams, Jones, and Jones,[119] of the Texas Station, fed more than 80 horses and mules, varying in age from weanlings to animals 20 years old, 1 pound of cottonseed meal daily in connection with other feeds for 224 days to two years, and in some cases, 2 pounds of cottonseed meal daily for a much longer period. The animals receiving cottonseed meal in their rations made larger gains and shed their old hair earlier in the spring than similar groups not receiving cottonseed meal.

One Percheron mare receiving one pound of cottonseed meal daily for 938 days and a standard-bred filly receiving two pounds daily from the time she became a weanling over a period of 686 days represented the highest levels of cottonseed meal feeding in the above investigation. The results of this study, the authors state, indicate that one or two pounds of 43% protein cottonseed meal would be a useful and valuable supplement to the rations commonly fed to horses and mules in the South.

In the Texas experiments, the heavy artillery horses that received cottonseed meal made a larger gain each year than did the control group fed the standard army ration of oats and prairie hay. Young mules and colts that were fed cottonseed meal from weaning time seemed to develop faster and weighed more at one year of age than did those failing to receive this

[117] W. J. Kennedy, E. T. Robbins, and H. H. Kildee, *Iowa Agr. Expt. Sta. Bull.*, **109** (1910).

[118] G. A. Bell and J. O. Williams, *U.S. Dept. Agr. Bull.*, **929** (1920).

[119] R. H. Williams, J. M. Jones, and J. H. Jones, *Texas Agr. Expt. Sta. Bull.*, **492** (1934).

supplement. Mares receiving two pounds of cottonseed meal were good sucklers and raised vigorous heavy foals.

The following feeding schedules [83] are suitable for the different classes of work stock.

1. Mares and Young Stock

A well-planned pasture program is necessary to provide grazing for brood mares and young stock. Good green pasture, supplemented with dry roughages, is sufficient to winter brood mares, colts and yearlings. Where only dry grass or low-quality roughage is available, there should be fed 1 to 1½ pounds of cottonseed meal or other protein concentrate daily per head to brood mares, and 1 pound per head daily to colts and yearlings.

If pasture is not available, 4 to 6 pounds of grain per head daily for brood mares, fed with good-quality hay or other roughage, will give good results. Foals, 6 to 12 months old, should receive 3 to 4 pounds of grain, and yearlings and 2-year-olds, 4 to 5 pounds of grain per head daily, in addition to good quality hay during winter months and dry periods when good pasture is not available.

Salt should always be available. It is a good practice to provide, also, a mixture of equal parts of steamed bone meal, ground limestone, or oyster shell flour, and salt—or a mixture of 2 parts of ground limestone and 1 part of salt.

2. Work Animals

Feeding the correct amounts of good-quality feeds at regular intervals during the work season helps to produce efficient power from the minimum amount of feed. A good plan is to divide the grain ration into two equal parts, fed morning and night. A good pasture near the barn, providing grazing at night and on idle days, helps to save feed. Some hay should be available also; if work stock are not on pasture, hay should be fed chiefly at night.

Idle work stock may be maintained on good pasture or roughage, but will work better if fed a light-work ration two to four weeks before starting heavy work.

The sets of rations given on page 865 are suitable for maintaining work animals.

G. Feeding of Poultry

An increasing amount of cottonseed meal is being used as a source of protein in rations of growing chickens and turkeys, and investigations that have been conducted by experiment stations have been of considerable value to poultry producers.

Berry,[120] of New Mexico, has found that cottonseed meal supplies

[120] L. N. Berry, *New Mexico Agr. Expt. Sta. Bull.*, **221** (1934).

Constituent of ration	Amount, pounds			
	No. 1	No. 2	No. 3	No. 4
Rations for Idle Stock				
Oats, corn, sorghum grain chops, or coarsely ground barley	2	0	0	0
Ear corn chops or grain sorghum head chops	0	2	2½	0
Cottonseed meal or cake	1	1	1½	1
Grass hay, or sweet sorghum fodder or hay	0	12	6	0
Grain sorghum fodder (with heads)	0	0	0	14
Legume hay	3	0	0	0
Cottonseed hulls, oat straw, or corn stover	9	0	6	0
Rations for Light Work				
Oats, corn, sorghum grain chops, or coarsely ground barley	5	0	0	4
Ear corn chops or grain sorghum head chops	0	6	6	0
Cottonseed meal or cake	1	1	1½	1
Grass hay, or sweet sorghum fodder or hay	0	11	5	0
Grain sorghum fodder (with heads)	0	0	0	12
Legume hay	3	0	0	0
Cottonseed hulls, oat straw, or corn stover	9	0	6	0
Rations for Heavy Work				
Oats, corn, sorghum grain chops, or coarsely ground barley	10	0	0	10
Ear corn chops or grain sorghum head chops	0	11½	11	0
Cottonseed meal or cake	1½	1½	2	1
Grass hay, or sweet sorghum fodder or hay	0	10	5	0
Grain sorghum fodder (with heads)	0	0	0	12
Legume hay	3	0	0	0
Cottonseed hulls, oat straw, or corn stover	8	0	5	0

very effectively, the added protein necessary for satisfactory growth when fed in a mash containing dried buttermilk. Ackerson and associates,[121] at the Nebraska Station, secured good results from the use of cottonseed meal in rations of growing chickens. Osborne and Mendel [122] studied the value of the amino acids of cottonseed flour for the growth of chicks and found that they were effective in promoting growth. Ringrose and Morgan,[123] at the South Carolina Station, found that cottonseed meal in the chick starting ration produced good growth when it replaced as much as three-fourths of the protein of meat scraps in a ration otherwise composed of yellow corn meal, wheat middlings, dried whey, and alfalfa leaf meal.

Cottonseed meal is often used as a source of protein in home-mixed laying mashes. Because dark yolks frequently result, when eggs from

[121] C. W. Ackerson, M. J. Blish, and F. E. Mussehl, *Nebraska Agr. Expt. Sta. Research Bull.*, **100** (1938).
[122] T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, **26,** 293 (1916).
[123] R. C. Ringrose and C. L. Morgan, *Poultry Sci.*, **17,** 109 (1938).

hens fed cottonseed meal are put in storage, it is recommended that the use of cottonseed meal be limited to mixtures for layers, whose eggs will be consumed fresh, and that it not exceed 6% of the total mash.[124]

Workers at the Texas Station [125] found that cottonseed meal and soybean oil meal may be used interchangeably in chick rations.

Ward and co-workers [83] have recommended the rations and procedures for feeding cottonseed meal rations to poultry in accordance with the present knowledge of research workers in this field. These will be given in detail in the following paragraphs.

For starter and growing mashes, the formulas given below are recommended (figures in pounds).[83]

Constituent	All-mash chick starter		Growing mashes	
	No. 1	No. 2	No. 1	No. 2
Yellow corn meal or sorghum grain chops	44	38	46	35
Finely ground oats or barley	10	4	12½	15
Wheat gray shorts or rice polishings	20	8	15	20
Wheat bran or rice bran	0	20	0	0
Cottonseed meal	6	8	12	10
Peanut meal or soybean meal	0	4	0	10
Alfalfa leaf meal	5	5	7	6
Meat scraps or fish meal	6	6	4	0
Dried milk (skim or buttermilk)	6	3	0	0
Ground limestone or oyster shell flour	2	2½	2	1
Bone meal or defluorinated phosphate	½	0	1	2
Salt	½	½	½	1
Cod-liver oil	⅛	1	0	0

1. Chickens

Feeding of the all-mash starter should be started when the chicks are 24 hours old and continued until they are 6 to 10 weeks old. A mixture of equal parts of milo or kafir chops, cracked wheat, and yellow corn chops is a good scratch grain, to be kept in feeders after the chicks are a month old. The all-mash chick starter designated above as No. 1 may be used as a broiler mash until the broilers are 10 or 12 weeks old, with small amounts of grain being added 2 to 4 weeks before they are marketed. If the chicks are raised for layers, pullets and cockerels should be separated early and the pullets kept on green range. The growing mash should be fed until the pullets are 5 months old. Scratch grain, oyster shell and grit, and clean water should always be available.

In laying rations, cottonseed meal should be limited to mixtures for layers whose eggs will be consumed fresh, and should not exceed 6% of the

[124] R. B. Thompson and C. A. Roberts, *Oklahoma Agr. Expt. Sta. Biennial Rept.*, p. 152 (1938).

[125] R. M. Sherwood and J. R. Couch, *Texas Agr. Expt. Sta. Bull.*, **569** (1939).

total mash; for it may cause dark yolks in eggs placed in storage. A practical laying mash, when eggs are not sold for cold storage, is: 70 pounds of a combination of any three available ground grains, mixed with the following 30-pound protein concentrate mixture—6 pounds, each, of alfalfa leaf meal and cottonseed meal; 10 pounds of peanut or soybean meal; 3 pounds of fish meal, meat scraps, or dried milk; 2 pounds, each, of bone meal and ground limestone; and 1 pound of salt.

If enough liquid skim milk or buttermilk is fed in clean troughs, dried milk may be omitted from chicken and turkey rations.

2. Turkeys [83]

For rapid gains, high finish, and best prices, turkey production requires full feeding of the animals from hatching time until sale. Turkeys should always have access to mash, turkey-size grit, fresh water, and ample green feed. Grain should always be kept in the feeders, or the flocks should be fed heavily each night. It is necessary to raise turkeys on clean ranges where chickens have not been kept, to change feeding grounds weekly, and to move the roosts frequently.

A good starter mash for poults is: 18 pounds of corn meal; 12 pounds of ground wheat or sorghum grain; 15 pounds of finely ground oats or barley; 8 pounds of wheat bran or rice bran; 8 pounds of alfalfa leaf meal; 20 pounds of cottonseed, soybean, or peanut meal; 12½ pounds of meat and bone scraps; 5 pounds of dried milk or whey, or dried brewers' yeast; 1 pound of ground limestone or oyster shell flour; ¼ pound of salt; and ½ pound of fortified cod-liver oil. A grain mixture may be kept before the poults, in a separate feeder, after the third week. The starter mash should be fed until the poults are 8 weeks old, when a gradual change should be made to the growing mash.

A suitable growing mash, to feed with grain, is: 100 pounds of a combination of any three ground grains, mixed with 8 pounds of alfalfa leaf meal; 8 pounds of meat and bone scraps; 15 pounds of cottonseed, peanut, or soybean meal; 2½ pounds of calcium supplement and ½ pound of salt.

III. Future Research

A review [126] of some of the experiment station work that has been conducted in recent years on the value of cottonseed products as a feed for livestock shows the wide use to which these feeds are adapted, and suggests many possibilities for future research to extend present uses and develop more uses. As our knowledge of amino acids, vitamins, and minerals is increased—to mention only three of the fields in which an increasing amount of research is being done—we shall have almost unlimited op-

[126] F. Hale and J. H. Baumgardner, *Proc. World Cotton Research Congress,* Waco, Texas (1941).

portunities to increase the efficiency and economy of the utilization of cottonseed feed products. The research worker can contribute much to the future economic importance of cottonseed products; and their present and potential economic and nutritional importance present a real challenge to the scientist.

CHAPTER XXII

MISCELLANEOUS PRODUCTS FROM SEED AND MEAL

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As indicated previously, the meal or residue from processing cottonseed for oil is principally used as an animal feedstuff. However, there are several minor uses of the meal or seed which are of some importance, or which may be expected to be of importance in the future.

I. Edible Products

The possibility of utilizing cottonseed on a large scale as a source of food for human beings is at present of considerable interest. This is so not only because cottonseed constitute a large potential source of high-protein foodstuffs for a world generally on somewhat short protein rations, but also because they are a rich source of certain vitamins and essential amino acids in which wheat and other cereal grains are naturally deficient.[1]

A. Cottonseed Flour[2]

The manufacture of cottonseed flour is carried out as follows. As a raw material, seeds are selected which are uniform in size and well filled, and which are free of field damage, of damage by insects, or deterioration through heating in storage. The use of seed containing more than 4–5% of immature kernels contributes an undesirable reddish color and a musty flavor to the finished product. Mechanical separation and rejection of immature meats after the seed are hulled is considered impracticable.

Cleaning and delinting of the seed is carried out in the usual manner; the delinted seed are recleaned and hulled in a bar huller, after which they are subjected to very thorough screening and air separation, to remove all but traces of the hulls.

[1] For a discussion of the nutritive value of cottonseed and other oilseed flours, in comparison with wheat and other cereal flours, see: T. F. Zucker and L. Zucker, *Ind. Eng. Chem.*, **35**, 868–872 (1943); D. B. Jones and J. P. Divine, *J. Nutrition*, **28**, 41–49 (1944); and W. F. Geddes, in M. B. Jacobs, ed., *The Chemistry and Technology of Food and Food Products*, Vol. I, Interscience, New York, 1944, pp. 680–684.

[2] Information in this section was furnished by C. W. McMath, Traders Oil Mill Co., Fort Worth, Texas, in a private communication to the author. See also C. W. McMath, in *Proc. 6th Cotton Research Congress*, Dallas, 1945, pp. 22–25.

The cleaned meats are rolled to a thickness of 0.007 to 0.010 inch, and cooked in a stack cooker at a temperature of about 225° F. for a period of one hour and ten minutes to one hour and forty minutes. In the cooker, the mass of hull-free flakes tends to become plastic and to flow more readily under pressure than do ordinary flakes containing some proportion of hulls. For this reason, the cooking operation is rather critical; the variables of time, temperature, and moisture content must be carefully adjusted in order to reduce the free-flowing character of the material sufficiently to permit pressing and at the same time yield a light-colored product.

Separation of the oil is effected in hydraulic presses, in the usual way. Upon removal from the presses, the hot press cake is cooled and then aged for 30 days before grinding.

Grinding is accomplished in hammer mills, with air separation of the fine material. The separators are so adjusted that 98% of the product will pass a 200 mesh sieve, this degree of fineness being essential for satisfactory baking qualities. Bolting of the flour through silk has not been found practicable.

A considerable proportion of the original material is rejected during the operation of grinding and separation. From a ton of average cottonseed that would produce 950 pounds of 43% protein meal, about 300 pounds of cottonseed flour is obtained.

The flour has a relatively light color, and a slight, pleasant, and characteristic nutty flavor. A typical analysis is given in Table 211.

TABLE 211

Composition of Cottonseed Flour

Proximate analysis	Per cent	Mineral	Per cent	Vitamin	μg/g.
Moisture	6.34	Phosphorus	1.26	Thiamin	10.4
Protein	57.53	Calcium	0.20	Riboflavin	10.2
Fat	6.45	Magnesium	0.65	Niacin	84
Fiber	2.06	Iron	0.012	Pantothenic acid	25.5
N-free extract	21.38	—	—	—	—
Ash	6.24	—	—	—	—

Use of the flour has been found advantageous in a variety of baked products and confections. Besides being a highly concentrated source of proteins of excellent biological quality, and of minerals and vitamins of the B group, it has certain unique physical properties which recommend it for special uses. It is considered to contribute to tenderness and shortness in certain baked products, and is particularly valued for its large water binding capacity in bakery and confectionery formulas of high-moisture

content. It is remarkably stable in storage, and is free of any tendency toward so-called "flavor reversion."

B. Other Edible Products

Heat treatment of cottonseed flour caramelizes the natural sugars present and causes the material to assume a deep reddish-brown color. This so-called thermoprocessed flour, marketed under the trade name of "Cinnacoa," has been widely used as a substitute for cocoa in baked products and confections, and has also found considerable use as a base for synthetic cinnamon. Other cottonseed products have been used as carriers for essential oils in the manufacture of synthetic black pepper and other spices.

Another edible cottonseed product, which has, however, so far been prepared only on an experimental scale, is "Poco-Nuts." This product consist of specially toasted whole cottonseed kernels.[3] They have a distinctive nutty flavor which is pleasing to most people and are less oily than most toasted nuts.

II. Technical Protein Products

Insofar as the author is aware, the use of cottonseed meal as a source of technical proteins has not passed the experimental stage. However, some interesting laboratory developments have been reported.

From cottonseed protein fractions, Gieger[4] has prepared a plywood glue which on $\frac{1}{16}$-inch birch gave a dry shearing test of 500 p.s.i. with 0–30% wood failure and a wet test (24 hours in water at room temperature) of 180 p.s.i. On hard maple, shearing tests of 2,200 p.s.i. with varying percentages of wood failure were obtained. For preparation of the protein fractions, Gieger[5] employs a novel method of leaching with salt solution, which is applicable to the uncooked and unextracted rolled flakes, and avoids the necessity of solvent extracting the oil to avoid heat denaturation of the proteins. The residue remaining after extraction of the protein may be dried, cooked, and pressed for oil recovery in the conventional way.

Rosenthal[6] has investigated the use of both cottonseed meal and cottonseed hulls as fillers in phenolic plastics. He found that the meal did not function merely as an inert filler, but could considerably influence the flow properties of the phenolic resin. A properly prepared composition consisting of equal parts of hulls, meal and resin was found to have good flow and cure time properties at 320–360° F., and to have a strength approaching that of commercial phenolic products. Its water absorption was but 0.8% in 24 hours.

[3] C. A. Smith, Perkins Oil Co., Memphis, Tenn., *private communication.*
[4] M. Gieger, *private communication.*
[5] M. Gieger, *Oil Mill Gazetteer,* **45,** No. 6, 7–11 (Dec., 1940).
[6] F. Rosenthal, *Ind. Eng. Chem.,* **33,** 980–983 (1941); **34,** 1154–1157 (1942).

Interest in cottonseed protein adhesives, plastics, fibers, etc., may be expected to increase after solvent-extracted cottonseed meal is available. In the past, the technical development of such products has been hampered by lack of a raw material which has not suffered some degree of heat denaturation in processing.

III. Carbohydrate Products

Cottonseed are the richest common source of the rare sugar, raffinose, which is used in the preparation of certain culture media.

According to Hudson and Harding,[7] and Englis *et al.*,[8] 2–4% raffinose may be obtained from commercial cottonseed meal.

IV. Fertilizers

In 1941, a total of 150,000 tons of cottonseed meal was used as a fertilizer in the United States.[9, 10] Of this amount, 137,000 tons was consumed as such and 13,000 tons was consumed in the manufacture of mixed fertilizers. Of the 137,000 tons consumed as such, 110,640 tons was used on cotton farms. The consumption in mixed fertilizers is generally much higher, being above 75,000 tons in both 1937 and 1939.[10] In the period 1928–1942, the highest amount consumed in any one year as a fertilizer on cotton farms was 468,000 tons, in 1932.[11]

The cottonseed meal used for fertilizer is naturally of low quality, and includes a certain amount of moldy or otherwise inedible meal.

Cottonseed meal and other oilseed meal fertilizers, although relatively expensive sources of plant food, are valued for certain special purposes. They are particularly used in garden fertilizer mixtures and for truck crops and tobacco grown in sandy soils from which inorganic fertilizers are inclined to leach badly. They decompose slowly in the soil and lack salinity and alkalinity. Cottonseed meal is popular as a fertilizer in Florida, in the sand belt soils of the East Coast, and in tobacco-growing regions generally. All tobacco fertilizers contain 10–20% of organic material.

Analyses of cottonseed meal, with respect to its plant food constituents, are to be found on pages 136 and 487.

Cottonseed meal is recommended as a particularly effective "fertilizer" for fish ponds.[12]

[7] C. S. Hudson and T. S. Harding, *J. Am. Chem. Soc.*, **36,** 2110–2114 (1914).

[8] D. T. Englis, R. T. Decker, and A. B. Adams, *J. Am. Chem. Soc.*, **47,** 2724–2726 (1925).

[9] U.S. Dept. Agr., Bureau of Plant Industry, Soils, and Agricultural Engineering. Circ. 689, *Fertilizer Consumption in 1941 and Trends in Usage.*

[10] U.S. Dept. Agr., *Agricultural Statistics,* 1944.

[11] U.S. Dept. Agr., Bureau of Agricultural Economics, *Farm Production, Farm Disposition, and Value of Cotton and Cottonseed, 1928–42.*

[12] See, for example, E. V. Smith and H. S. Swingle, *Trans. Am. Fisheries Soc.*, **72,** 263–266 (1942).

CHAPTER XXIII

COTTONSEED HULLS

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I. Introduction

We are living in an era in which economic survival demands wringing the ultimate values from any raw material. Cottonseed, itself, at one time was an industrial waste. During the past one hundred and fifty years, however, improvements in technology have enabled the oil miller, as well as the farmer, to realize a profit in the processing of cottonseed—a profit dependent upon the sale of not one but four major products: oil, cake or meal, linters, and hulls.

For many years, hulls were thrown away or burned as fuel by the mills. Many individuals still consider the hulls an industrial waste, although for more than half a century they have been used extensively and profitably as a roughage in livestock rations. It is true that the technology of oil, meal, and linters has far outdistanced the technology of cottonseed hulls. Because of this, oil millers have repeatedly called for a thorough investigation of the industrial potentialities of the hulls. Bass and Olcott [1] stated that in 1885 cottonseed hulls began to be used extensively as roughage for livestock; hulls were used in the construction of miniature golf courses in 1925; xylose was produced on a pilot-plant scale from cottonseed hulls in 1929; a sweeping compound based on cottonseed hull bran was developed in 1938; and a highly effective activated carbon was produced from hull bran in 1939. Yet, with all due respect to the individuals and laboratories that have devoted much valuable time and energy to these developments, it is doubtful that more than a very small fraction of the cottonseed hulls produced in this country have been or are being diverted into these industrial channels.

The primary purpose of this discussion is to ascertain the technological and economic reasons behind the apparent retarded use of cottonseed hulls as an industrial raw material, a situation which centers largely on

[1] L. W. Bass and H. S. Olcott, *Ind. Eng. Chem., News Ed.*, **18**, 139–142 (1940).

the value of cottonseed hulls as a livestock roughage compared to the value of hulls as an industrial raw material. Another way of visualizing this problem is to consider the dairy cow or beef steer as a production unit competing with chemical industries for the use of a specific raw material. As background for this discussion, the chemical and physical characteristics, availability, and costs of cottonseed hulls must be known; similar raw materials that might be competitive with them must be examined; and the suggested industrial uses for them must be reviewed.

II. Physical and Chemical Characteristics

A. Physical Properties

Cottonseed hulls are bulky. They weigh approximately 10 pounds per cubic foot, the density depending upon the degree of delinting and the degree of packing. The hull is a horny material which forms the external covering that encloses and protects the seed kernel or meat. Cotton fiber is an outgrowth from an outer layer of cells of the hull. This fiber is held fast between relatively large cells of the hull, exterior to the cotton fiber cells.

B. Chemical Composition

Chemically, cottonseed hulls consist of three major components: pentosan, cellulose, and lignin. Anderson *et al.*[2] has made an extensive study of the pentosan fraction of cottonseed hulls. They report that it is a condensation product of a polyuronide of D-glucuronic acid and D-xylose in which 1 molecule of the acid is combined with from 10 to 16 molecules of the sugar. Xylose, then, would be the only sugar anticipated, upon hydrolyzing the pentosan fraction of cottonseed hulls.

Cellulose is a condensation product of the six-carbon sugar, dextrose, the trade name of which is corn sugar or Cerelose. Dextrose, or glucose as it is sometimes called, exists in two different space configurations: α-glucose and β-glucose. The glucose derived from starch and maltose has the α-space configuration. Starch and maltose are fermented by yeast to alcohol. The glucose derived from cellulose and cellobiose (the equivalent of maltose) has the β-configuration. These two latter compounds are not fermented by yeast, even though the glucose derived from them is fermentable. In order to produce a yeast-fermentable sugar from cellulose, therefore, the cellulose must be completely degraded to the monosaccharide, glucose, and must not be permitted to revert or condense to a polysaccharide.

Cellulose prepared from cottonseed hulls is similar to the cellulose prepared from other sources. In addition, however, it may be separated

[2] E. Anderson, J. Hechtmann, and M. Seeley, *J. Biol. Chem.*, **126,** 175–179 (1938).

into two fractions, depending upon fiber length. The cellulose obtained from the lint or hull fiber part of the hulls is of narrow fiber diameter and about ⅛ inch long. The cellulose obtained from the bran fraction of the hulls is also of narrow fiber diameter but is extremely short.

The third component, lignin, is the insoluble residue remaining after treating cellulosic materials with 72% sulfuric acid.

High and low values for the analysis of cottonseed hulls which are taken from several different sources [3-6] are reported in Table 212. The

TABLE 212

Chemical Analysis of Cottonseed Hulls

Component	Per cent by weight, oven-dry basis		
	Average	Low	High
α-Cellulose	43.9	42.0	46.6
Cross and Bevan cellulose	46.9	35.1	53.40
Pentosans	29.5	22.3	38.40
Lignin	21.95	17.5	25.0
Ash	1.79	—	—
Protein	3.30	—	—
Crude fiber	49.18	—	—
Acetic acid by hydrolysis	4.98	—	—
Alcohol-benzene extract	5.1	—	—

average values computed from these various sources and included in Table 212 are not specific to any particular sample. That these values are undoubtedly high is evidenced by the fact that the percentages of α-cellulose, pentosan, lignin, ash, protein, and alcohol–benzene extract total more than 105%. The average values are indicative only, and should be used with reservation.

It is observed that the analytical values in Table 212 vary considerably. The variation in chemical composition of hulls is due to many different factors: the original seed, locality, climate, soil, time of picking of the cotton, conditions of storage, degree of delinting, and the methods of analysis.[4] The author has worked with different samples of cottonseed hulls which ranged in α-cellulose content from 35–47%, in pentosan content from 19–27%, and in lignin content from 15–20%.

The degree of delinting is a factor that must be given special consideration. A sample of hulls obtained from seed from which neither a first- nor a second-cut lint has been removed, may analyze 40% α-cellulose. A sample of hulls from the same seed, after removal of first- and second-

[3] J. W. Dunning and E. C. Lathrop, *Ind. Eng. Chem.*, **37,** 24–29 (1945).
[4] A. P. Sakoshchikov, V. T. Ivanova, and A. M. Kurennova, *Ind. Eng. Chem., Anal. Ed.*, **6,** 205–208 (1934).
[5] W. H. Baldwin and J. A. LeClerc, *Oil & Soap,* **16,** 178–180 (1939).
[6] Q. O. Chemical Co., Memphis, Tenn., *private communication.*

cut lint, may analyze 36% α-cellulose. The pentosan and lignin contents of the hulls increase correspondingly with the decrease in α-cellulose content, because of the removal of linters. The history of a sample of hulls must be known, therefore, before any value can be attached to its analysis.

1. Composition of Different Fractions

The change in chemical composition of cottonseed hulls because of mechanical treatment is most pronounced when the hulls are ground and separated by air or water for the production of hull fiber and hull bran. Smith and Purves [7] report that the pentosans in a sample of cottonseed hulls may be concentrated from 27% in the original hulls to 34% in the coarse bran fraction. By grinding and gravity separation, they may be divided into two fractions, each having a chemical composition different from the parent material. One fraction, the hull fiber, is richer in cellulose and poorer in pentosan than the original hulls. The other fraction, the hull bran, is richer in pentosan and poorer in cellulose than the original hulls. This unique characteristic of cottonseed hulls has been put to use by several cottonseed mills in this country in producing a hull fiber that is valuable as a source of α-cellulose. The bran obtained from the process is used in mixed feeds or may be used in various chemical processes. Normally, the hull fiber produced in defibering mill-run hulls analyzes 50–55% α-cellulose. The α-cellulose content of hull fiber may be increased to 70% by thoroughly cleaning the fiber for removal of "pepper." Approximately 200 pounds of hull fiber and 1,700 pounds of hull bran may be produced from a ton of mill-run cottonseed hulls.

2. Comparison with Other Cellulose-Bearing Materials

Cottonseed hulls belong to an enormous group of cellulose-containing materials termed "agricultural residues." Several of these agricultural residues are collected at industrial processing plants and for convenience may be termed "collected agricultural residues." In this latter group are cottonseed hulls, corncobs, oat hulls, sugar cane bagasse, flax shives, hemp hurds, peanut shells, cottonseed burrs, and rice hulls. Since all these residues are annually collected in local plants in amounts ranging from hundreds to thousands of tons, and since they are all cellulose-pentosan-lignin-containing materials, they may all be in competition with one another for any one industrial use. It must be realized, however, that each of these collected agricultural residues has more or less distinctive physical and chemical properties. The chemical analyses of representative samples of cottonseed hulls and other cellulose-containing materials are given in Table 213. It may be seen that the pentosan, cellulose, and lignin content of agricultural residues varies somewhat from one residue to another.

[7] M. A. Smith and C. B. Purves, *Ind. Eng. Chem., Anal. Ed.*, **13,** 157–159 (1941).

The chemical analyses of ponderosa pine, a typical softwood—and tanbark oak, a typical hardwood—have been included in Table 213 in order to compare their chemical composition with that of agricultural residues. These data indicate that the amounts of pentosan in cottonseed hulls, corncobs, oat hulls, sugar cane bagasse, and flax shives are considerably higher than the amount of pentosan in the softwood Ponderosa pine and slightly higher than the amount of pentosan in the hardwood Tanbark oak. On the other hand, the amounts of cellulose in the five agricultural materials are lower than the amount of cellulose in either the soft- or hardwood. Rice hulls, cottonseed burrs, peanut shells, and hemp hurds, which are not listed in Table 213, have a much lower pentosan content but about the same cellulose content as the other collected residues.

TABLE 213

Analyses of Cellulose-Bearing Materials[a]

Residue	Per cent by weight, air-dry basis		
	Pentosans	Cellulose	Lignin
Cottonseed hulls	21.0	35.1	16.8
	29.5[b]	43.9[b]	21.95[b]
Corncobs	28.1	36.5	10.4
Oat hulls	29.5	33.7	13.5
Sugar cane bagasse	20.4	41.3	14.9
Flax shives	23.0	38.0	24.0
Ponderosa pine	7.4	52.3	26.6
Tanbark oak	19.6	44.8	24.8

[a] J. W. Dunning and E. C. Lathrop, *Ind. Eng. Chem.*, **37,** 24–29 (1945).
[b] Taken from Table 212.

Some agricultural residues have special properties that make them a preferred raw material for the manufacture of certain products. For example, sugar cane bagasse is preferred for the manufacture of insulating building boards, and wheat straw is preferred for the manufacture of 9-point corrugating box board. For chemical purposes, however, several of the agricultural residues are interchangeable. For this reason, the cost of an agricultural residue delivered to an industrial plant is one of the major factors controlling the use of agricultural residues by the chemical process industries.

III. Economic Considerations

The quantity of cottonseed hulls produced during each season from 1919 to 1945 and the value of those hulls are given in Table 214. The quantity of cottonseed hulls produced in each state for the year ending

TABLE 214

Quantities and Prices of Cottonseed Hulls[a]

Year[b]	Quantity, 1000 tons	Value, dollars per ton	Year[b]	Quantity, 1000 tons	Value, dollars per ton
1945	984	13.22	1931	1304	8.02
1944	927	12.80	1930	1384	8.75
1943	1085	8.72	1929	1368	9.39
1942	992	7.97	1928	1320	7.56
1941	1107	7.92	1927	1854	4.79
1940	1055	8.27	1926	1547	8.17
1939	1161	6.19	1925	1331	10.33
1938	1626	5.49	1924	941	13.53
1937	1144	9.13	1923	944	12.93
1936	988	6.65	1922	937	9.54
1935	913	11.23	1921	1256	8.01
1934	1103	6.81	1920	1143	9.69
1933	1312	3.57	1919	1137	15.78
1932	1511	3.46			

[a] From reports of U.S. Bureau of the Census.
[b] Season ending July 1.

TABLE 215

Quantities and Value of Cottonseed Hulls Produced in Different States in 1940[a]

State	Quantity	Value, dollars per ton	State	Quantity	Value, dollars per ton
Alabama	61,128	10.30	North Carolina	37,049	9.04
Arizona	25,258	7.01	Oklahoma	37,713	9.49
Arkansas	116,277	7.53	South Carolina	56,799	9.37
California	35,624	7.34	Tennessee	89,883	6.53
Georgia	108,214	10.12	Texas	248,564	8.54
Louisiana	54,218	8.91	All other states	26,050	6.19
Mississippi	158,001	7.06			

[a] From reports of the U.S. Bureau of the Census.

TABLE 216

Production and Surplus of Hulls in "Surplus" Areas[a]

Locality	Hulls produced, tons	Local surplus, tons
Northwest Mississippi	110,000	82,500
Northeast Louisiana	16,500	11,500
Eastern Arkansas	55,000	33,000
West Tennessee	96,250	48,000
Southwest Missouri and Cairo, Illinois	35,750	26,750

[a] Data from the National Cottonseed Products Association, privately communicated to the author.

July 1, 1940, and their value are given in Table 215.[8] The year 1940 was selected because of the abnormality of more recent years, due to World War II.

For the years 1919 through 1945, the average yearly production of cottonseed hulls for the United States was 1,198,888 tons, having an average value of $8.81 per ton. Even though cottonseed hulls may be considered an agricultural waste, most of the hulls produced in this country find an outlet in the animal feeding industry. There is, therefore, actually very little surplus of hulls, in the sense that any appreciable quantity is unused. Considerable variation in demand for hulls from region to region, however, does exist.

In the southeastern states (North and South Carolina, Georgia, Florida, and Alabama), the demand for roughage generally exceeds production and hulls are usually shipped in from other areas. In the Southwest (Texas and Oklahoma), a similar situation exists. The western states (New Mexico, Arizona, and California) consume all the hulls they produce. Production exceeds local consumption only in the Mississippi Valley States. This condition exists only in the parts of these states where the numbers of livestock are small compared to hull production.[9]

Estimates of the quantities of hulls produced and hulls consumed within the territories which have a "surplus" of hulls are given in Table 216.

The quantities of hulls produced are reasonably accurate but the quantities of "surplus" hulls in local areas are subject to a wider range of error. This "surplus" will, of course, vary from year to year depending upon several factors, including the supply of other roughages in local and adjacent areas, and the demand for hull fiber and hull bran. It must be emphasized that the word "surplus" is used in the sense that local supply exceeds local demand. Surplus hulls, therefore, usually are not waste.

The greatest concentration of hull production is at Memphis, Tennessee, where approximately 80,000 tons are produced annually.[9] Local feeding demand is relatively small, absorbing about 15% of the production. Memphis mills process about one-third of the total production into fiber and bran.

The data in Table 216 indicate that of the 1,198,888-ton average annual production of cottonseed hulls only 201,750 tons may be considered "surplus." In general, these hulls accumulate in relatively small tonnages in specific localities over the country.

The foregoing information indicates that approximately 85% of the hulls produced in this country are normally consumed in the localities in which they accumulate. The remaining 15% of the hulls accumulate in

[8] Department of Commerce, Bureau of the Census, Washington, D. C.
[9] National Cottonseed Products Association, *private communication.*

areas in which the local demand does not consume the supply. Depending upon the year, approximately 50% of these "surplus" hulls are shipped to nearby consumer markets, leaving scattered small tonnages of hulls that actually may be waste.

IV. Potential Industrial Uses

The potential industrial uses for cottonseed hulls that are described in the literature may be classified into two groups. Group 1 comprises those uses in which the hulls are employed as a bulk material without previous chemical treatment. Group 2 comprises those uses in which the several constituents in the hulls are altered by chemical means before use.

A. Bulk Uses

1. Use as an Animal Feed

The largest use for cottonseed hulls has been as a source of roughage in dairy cattle, beef cattle, sheep, and work stock feeds. The bulky nature of hulls makes them especially suitable for mixing with concentrates in feeding dairy cattle. Since concentrates are inclined to become heavy when moistened, the addition of hulls keeps such a mixture porous and thus more easily reached by the digestive juices.

Although it is out of place in this chapter to discuss the use of cottonseed hulls in feeds in detail, certain data regarding their value is warranted, since this represents their largest and most profitable outlet.

Lloyd [10] found cottonseed hulls to be slightly superior, pound for pound, to corn silage for fattening four-year-old beef steers. Jones *et al.*[11] showed that sorgo silage and sorgo fodder were more satisfactory roughages than cottonseed hulls when fed with ground milo heads and cottonseed meal for fattening calves. Shealy and Gratz [12] reported that sorghum silage, peanut hay, and cottonseed hulls had about the same feeding value. Buchanan [13] found that cottonseed hulls were superior to corn silage, sorghum silage, and sagrain silage. Lush [14] reported that cottonseed hulls were superior to hill land carpet and Bermuda grass hay, and almost equal to high-quality Bermuda, but inferior to mixed clover hay for milk production.

There have been several attempts to increase the food value of cottonseed hulls and other cellulosic materials by treating them with acids, alkalis, and other reagents.[15, 16] Although many of these attempts are theo-

[10] E. R. Lloyd, *Mississippi Agr. Expt. Sta. Bull.*, **167,** 3–8 (1914).
[11] J. M. Jones, W. H. Black, and F. E. Keating, *Texas Agr. Expt. Sta. Bull.*, **363,** 1–36 (1927).
[12] A. L. Shealy and L. O. Gratz, *Florida Agr. Expt. Sta. Bull.*, **320,** 1–10 (1938).
[13] D. S. Buchanan, *Mississippi Agr. Expt. Sta. Bull.*, **278,** 2–11 (1930).
[14] R. H. Lush, C. H. Staples, J. L. Fletcher, and S. Stewart, *Louisiana Expt. Sta. Bull.*, **238,** 1–8 (1933).

retically sound, in that the crude fiber of the cellulose material may be degraded and the digestibility of its constituents increased, these methods have not been economically successful in the United States.

2. Use as a Soil Conditioner

The bulky nature of cottonseed hulls makes them an excellent soil conditioner. Their lignin and carbohydrate content tends to build up the humus content of soil. In addition, the small amount of nitrogen and the slowly available metallic salts in hulls give them some fertilizer value.

TABLE 217

Base Exchange Capacity of Various Materials[a]

Material	Base exchange capacity	Material	Base exchange capacity
"Natural humus"	1.73	Dehydrated manure	0.73
German peat moss	1.43	Barr bog peat	0.66
"Hyper-humus"	1.39	Cottonseed hull bran[b]	0.40
Leaf mold	1.18	Cottonseed hulls[b]	0.38
Sphagnum moss	1.12	Cow dung, dried 105°C.	0.24
Michigan peat	1.07	Bagasse	0.13
Brown rot	1.07	Rye straw	0.00
Oak leaves	0.95	Wood shavings	0.00

[a] G. F. Muller, *Doctoral Thesis,* Rutgers Univ., 1930.
[b] From D. M. Musser and R. F. Nickerson, *Ind. Eng. Chem.*, **31,** 1229–1232 (1939).

The ash of cottonseed hulls, which contains large amounts of calcium, magnesium, potassium, some phosphorous and the trace elements, has proven to be a satisfactory fertilizer, particularly as a source of potassium. It has been stated [17] that 1 ton of hull ashes is equivalent to 4.5 tons of average hardwood ashes and to 15 tons of leached hardwood ashes. Anderson *et al.*[18] found that cottonseed hull ashes were no better than other sources of potassium for growth of tobacco. It was observed that the use of hull ashes did not result in the accumulation of undesirable salts in the soil.

The base exchange capacity of cottonseed hulls and hull bran has been investigated at the Mellon Institute.[19] Results of these investigations and comparable values by Muller [20] for a variety of other organic materials, in milliequivalents per gram of dry weight, are given in Table 217.

[15] J. G. Archibald, *J. Agr. Research,* **27,** 245–265 (1924).
[16] V. T. Ivanova, and A. M. Kurennova, *Trest Khlopkochistitel Prom.* (Cotton Ind. Trust), **1,** 115–124 (1933); *Chem. Abst.,* **28,** 5148 (1934).
[17] S. P. Sadtler and L. J. Matos, *Industrial Organic Chemistry,* Lippincott, Philadelphia, 1923, p. 89.
[18] P. J. Anderson, T. R. Swanback, and O. E. Street, *Connecticut Agr. Expt. Sta. Bull.,* **386,** 574–578 (1936).
[19] D. M. Musser and R. F. Nickerson, *Ind. Eng. Chem.,* **31,** 1229–1232 (1939).
[20] G. F. Muller, *Doctoral Thesis,* Rutgers Univ., 1930.

The appreciable base exchange of cottonseed hulls and hull bran suggests their use as a litter material for domestic animals. Pine and other oils may be mixed with the hulls to prevent their clinging to the animals. The soiled bedding with its nitrogenous manure then makes an excellent fertilizer and soil conditioner.

3. Use in Phenolic Plastics

Cottonseed hulls have been suggested as a filler for phenolic molding compounds. Hurst [21] obtained a patent on a low-cost molding compound suitable for producing an infusible product. He recommends mixing not more than 30% of a synthetic resin, such as phenol-formaldehyde with the hulls.

Rosenthal [22] took exception to the claim made by Hurst regarding the nonabsorbency of the cottonseed hull filler, citing the work of Meharg.[23] Meharg found that one of the six primary requirements for a plastics filler is the ease with which the filler is wetted by the resin. Rosenthal, therefore, prepared plastic materials compounded from hull bran samples which were ground to particle sizes ranging from 40-mesh to finer than 200-mesh. Molding compounds were made by impregnating each of the samples with the same amount of identical phenolic resin. Compounds were also prepared from bran of increasing particle sizes containing 5, 10, 15, and 20% hull fiber, respectively. It was found that the absorbing power of the cottonseed hulls was a function of their particle size and fiber content. A maximum impact strength was obtained when the cottonseed hull filler had a particle size of 100-mesh and contains 10% fiber. Rosenthal found that the control of particle size and fiber content of ground cottonseed hulls permits the preparation of phenolic cottonseed hull compounds whose strength characteristics compare favorably with commercial phenolic compounds. He states further that the versatility of comminuted cottonseed hulls with respect to particle size and fiber content is a unique characteristic which tends to increase the scope of the potential application of cottonseed hulls as a filler in phenolic compounds. In 1944, Rosenthal [24] was granted a patent which covered the use of cottonseed hulls in molding compounds. According to his patent, cottonseed hulls are ground in a hammer mill or Wiley mill and then impregnated with less than 20% of a phenolic resin, after which the mixture is dehydrated at approximately 140° F. The mixture is then placed between the platens of a press and cured at a temperature of 170° F. and at 2,000 p.s.i. The board thus prepared hardens and shows great mechanical strength and resistance to flexure.

[21] I. A. Hurst (to General Electric Co.), U.S. Pat. 1,863,540 (1932).
[22] F. Rosenthal, *Ind. Eng. Chem.*, **33,** 980–983 (1941).
[23] V. Meharg, *Modern Plastics,* **16,** 30 (Oct., 1938).
[24] F. Rosenthal (to Univ. Tenn. Research Corp.), U.S. Pat. 2,346,943 (1944).

An editorial note in the Experiment Station Record [25] states that: "A simple low-cost plastic material from (hull) bran for manufacture of sheaves for textile looms has been proved by the Tennessee (Agricultural Experiment) Station and developed in a commercial molding plant. Several hundred thousand of these sheaves already are in practical use and are demonstrating their superiority to those made from other plastics."

4. Miscellaneous Bulk Uses

There are innumerable suggested uses for cottonseed hulls and cottonseed hull bran which might provide small tonnage outlets for hulls in the localities in which they accumulate. They have been suggested as an excelsior substitute, and for horse collar and baseball stuffing.[26] Various sweeping compounds employing a base of hulls have been recommended and several are in use, at least in local areas. Olcott [27] describes a sweeping compound consisting of 95.6% cottonseed hull bran and 4.4% paraffin oil, which was superior to the commercial sawdust product tested. About twenty years ago, a patent [28] was granted to cover the use of cottonseed hulls for the construction of putting greens. They are occasionally used for this purpose on golf courses in arid regions. During the period in which miniature golf was a fad, considerable quantities of hulls were used for the construction of courses. Hulls are also being used to a small extent in local road construction for covering newly poured concrete, since they will retain moisture longer than most similar materials. Hulls have also been used in tar mixtures for calking the expansion joints of roadways. During the summer of 1937, cottonseed hulls came to the aid of western farmers in their fight against grasshoppers.[29–31] The hulls were ground up very fine and mixed with poison. This mixture was spread over the fields in "hopper-infested areas," in some instances by planes. Hulls, being very light, proved to be good poison carriers.

Hulls have been suggested as a strawberry mulch [32] and a sweet potato storage medium.[33] Because of their low density, hulls have been used locally as an insulating material between studs and over ceilings in the construction of houses. Although ammonium sulfate and similar fire-retardent compounds may be used to fireproof the hulls, further work on rodent proofing and other phases of the problem must be conducted before the use of hulls as an insulating material becomes significant.

[25] *Expt. Sta. Record,* **87,** 1 (1942).
[26] A. W. Boynton, U.S. Pat. 288,766 (1883).
[27] H. S. Olcott, *Soap,* **14,** 105–107 (1938).
[28] T. M. Fairbairn, A. S. Valdespino, and R. McCart, U.S. Pat. 1,559,520 (1925).
[29] R. E. Hutchins and C. Lyle, *J. Econ. Ent.,* **31,** 319 (1938).
[30] F. A. Fenton, *American Cotton Grower,* **3,** 37 (1937); *Cotton Literature,* **7,** 422 (1937); *Oklahoma Agr. Expt. Sta. Bull.,* **233,** 1–12 (1937).
[31] A. L. Ward, *Cotton and Cotton Oil Press,* **39,** No. 31, 3 (1938).
[32] A. B. McKay, *Mississippi Agr. Expt. Sta. Bull.,* **26,** 1–15 (1893).
[33] F. S. Shiver, *South Carolina Agr. Expt. Sta. Bull.,* **28,** 1–15 (1897).

B. Chemical Uses

Cottonseed hulls contain pentosans, cellulose, lignin, tannins, inorganic salts, and various pigments and resins. By treatment of these constituents with chemicals under different conditions, a variety of products may be obtained.

1. Hulls as a Source of Tannins

The tannins and some of the ash, pigments, and resins may be extracted from cottonseed hulls with hot water.[34] These tannins are reported to be suitable for use in industrial tanning solutions.

2. Hulls as a Source of Cellulose

Pentosans, the condensation product of xylose, and cellulose, the condensation product of dextrose, respond to several different types of chemical treatment. Cellulose is insoluble in hot dilute alkali. Pentosans are soluble, but not completely, in cold 5% sodium hydroxide. Lignin is slightly soluble in cold alkali and quite soluble in hot alkali. The cellulose fraction of cottonseed hulls, therefore, may be obtained more or less pure by cooking the hulls in hot dilute sodium hydroxide. This cooking removes the major part of the pentosans and lignin. After bleaching, a white cellulosic product is obtained.

This general procedure is the basis of two patents [35, 36] for preparing cellulose from cottonseed hulls for use in viscose manufacture. To give one specific example, Golova [37] cooks cottonseed hulls with six parts of 3–6% sodium hydroxide at 130–150° C. for four to seven hours. The resultant material after thorough washing is given a two-stage bleaching.

Some investigators separate the hulls into hull fiber and hull bran, and use only the hull fiber for the preparation of cellulose. This procedure, although losing much cellulose to the hull bran, yields a more uniform cellulose with less drastic treatment. Golova [38] states that hull fiber is as satisfactory as cotton linters for the manufacture of viscose and gives a rayon similar in appearance and texture to cuprammonium rayon.

Although the standard sulfate and sulfite pulping methods may be applied to cottonseed hulls, the alkali method has received most attention. This is quite reasonable since the presence of the hull fiber, a rather pure cellulose, in the presence of the cellulose in the bran fraction provides

[34] A. P. Zakoshchikov, V. T. Ivanova, G. A. Korzheniovskii, and A. M. Kurennova, *Trest Khlopkochistitel Prom.* (Cotton Ind. Trust), **1,** 102–115 (1933); *Chem. Abst.*, **28,** 5280 (1934).

[35] O. Muller (to Eheinische Kunstseide-Fabrik), U.S. Pat. 930,874 (1909).

[36] F. W. Stockton, U.S. Pat. 1,295,078 (1919).

[37] O. P. Golova, *Iskusstvennoe Volokno,* **5,** No. 6, 10–19 (1934); *Chem. Abst.*, **29,** 1626 (1935).

[38] O. P. Golova, *Kunstseide,* **17,** 302–307 (1935); *Chem. Abst.*, **30,** 2751 (1936).

a heterogeneous raw material. The drastic treatment necessary to purify the cellulose of the bran tends to degrade the cellulose of the fiber.

Korzheniovskii [39] recommends the nitric acid pulping method for cottonseed hulls. According to this procedure, the hulls are given a preliminary cook with hot dilute nitric acid prior to cooking with hot dilute sodium hydroxide. Korzheniovskii has found that this procedure yields a higher quality cellulose than the straight alkali, sulfate, or sulfite extractions.

Methods involving the production and purification of cellulose from hull fiber are in commercial use. Methods for producing cellulose from the hull have not received industrial acceptance.

3. Separation of Xylose, Dextrose, and Lignin

The pentosan and cellulose fractions of cottonseed hulls may be degraded to the monosaccharides, xylose and dextrose, respectively. Here again the two constituents react differently to chemical treatment. The pentosans are hydrolyzed to xylose by hot dilute mineral acids. Under certain conditions, only a small part of the cellulose is hydrolyzed to dextrose. Cellulose, on the other hand, requires more drastic treatment for the production of dextrose. Cellulose may be degraded to dextrose by cooking at elevated temperatures in the presence of dilute acid, or by treating with concentrated mineral acids followed by cooking in hot dilute acids.

Lignin is not soluble in either cold concentrated mineral acids or in hot dilute acids. It follows, therefore, that the three major constituents of cottonseed hulls may be separated into three fractions by different hydrolytic procedures. The pentosans may be hydrolyzed to xylose, leaving the cellulose and lignin combined in a solid residue. The cellulose may then be hydrolyzed to dextrose, leaving the lignin as a solid residue.

4. Carbohydrates from Hulls

(a) Production of Xylose from Pentosans. In 1930, Hall *et al.*[40] of the Bureau of Standards published their preliminary investigations upon the yields of xylose from cottonseed hull bran and peanut hulls. In the same year, Schreiber *et al.*[41] described a semicommercial production of xylose. The essential operations of this process were: (*a*) pretreatment of the bran, (*b*) extraction of the xylose with dilute sulfuric acid, and (*c*) processing of the extract to obtain crystalline xylose.

The bran was first cooked with water at 15 p.s.i. pressure for two hours,

[39] G. A. Korzheniovskii and R. L. Raskina, *Trest Khlopkochistitel. Prom.* (Cotton Ind. Trust), **1,** 124–147 (1933); *Chem. Abst.*, **28,** 5227 (1934).

[40] W. L. Hall, C. S. Slater, and S. F. Acree, *Bur. Standards J. Research,* **4,** 329–343 (1930).

[41] W. T. Schreiber, N. V. Geib, B. Wingfield, and S. F. Acree, *Ind. Eng. Chem.*, **22,** 497–501 (1930).

drained, soaked in 0.25 *N* sulfuric acid, drained, and thoroughly washed with water. This pretreatment removes the gum and ash that interferes with the subsequent crystallization of xylose. The pentosans were then hydrolyzed to xylose by cooking the pretreated hull bran for two hours at 10 p.s.i. pressure in 0.2 *N* sulfuric acid. The liquid:solid ratio used in the extraction of pentosans was 3:1. The extract was used several times to build up the xylose concentration in the extract of 15%. The sulfuric acid in the extract was then neutralized with lime to a *p*H of 2.8. After removal of the precipitated calcium sulfate by filtration, the extract was evaporated under reduced pressure to a specific gravity of 1.28, filtered, and evaporated further to a specific gravity of 1.35 for the crystallization of xylose. The cost of heat, power, water, and chemicals for the process was calculated to be $0.02343 per pound of crystalline xylose.

(b) Saccharification of Cellulose to Dextrose. Although very little work has been done on the hydrolysis (saccharification) of the cellulose fraction of cottonseed hulls, there is a voluminous literature on the hydrolysis of the cellulose in other raw materials from which selected references may be cited.[3, 42, 43] There are two methods of cellulose saccharification which may be briefly described to illustrate the general procedures involved. Bergius [42] hydrolyzes cellulose with 42% hydrochloric acid at room temperature in a diffusion battery. The concentrated hydrochloric acid in the extract is distilled at reduced pressure and subsequently fortified with hydrogen chloride gas for reuse in further extractions. The solid carbohydrates remaining after distillation of hydrochloric acid are dissolved in water and cooked for a short time to yield dextrose.

The modified Scholler process,[43] developed by the Forest Products Laboratory, makes use of the hydrolytic activity of dilute sulfuric acid at elevated temperatures. In this process, a reaction vessel is charged with the cellulosic material to be hydrolyzed. Upon packing the raw material in the vessel with live steam, sulfuric acid of 1.0 to 2.0% concentration at a temperature of about 150° C. is admitted to the reactor. After a reaction period of approximately twenty minutes, the extract is blown from the kettle and more dilute acid is admitted. The sulfuric acid for the succeeding cycles is reduced to 0.5 to 0.6% in concentration, and the temperature is increased about 5° C. per cycle, until a temperature of 185° C. is attained. The remainder of the run is maintained at about 185° C. From 13 to 18 cycles are required to exhaust the raw material of cellulose.

5. Utilization of Lignin

In all of these saccharification processes, a solid lignin residue remains. There has been considerable discussion concerning the value of this lignin.

[42] F. Bergius, *Zellstaff Faser*, **32,** 50–56 (1935); *Chem. Abst.*, **29,** 5687 (1935).

[43] E. E. Harris, E. Beglinger, G. J. Hajny, and E. C. Sherrard, *Ind. Eng. Chem.*, **37,** 12–23 (1945).

It has been suggested for use as a plastics filler [44] and a soil conditioner.[45] It may be converted into vanillin and other chemicals.[46] Regardless of the many technical papers describing the industrial potentialities of lignin, there remains to be found a single large tonnage use for it except as a fuel.

6. Production of Furfural

Through a system of hydration and dehydration reactions, pentosans may be converted into furfural. The Quaker Oats Company, at Cedar Rapids, Iowa, has operated a furfural production plant for some years employing oat hulls as the raw material.[47, 48] In brief, their process consists of cooking oat hulls moistened with 5% sulfuric acid in spherical digesters. Steam at about 60 p.s.i. pressure is passed through the oat hulls to remove the furfural as it is formed. The steam–furfural mixture is then fractionated to recover the furfural. The Q. O. Chemical Company, in Memphis, Tennessee, follows this same operation. This plant has the capacity to produce 10,000 to 15,000 tons of furfural a year and requires about 100,000 tons a year of raw material. It was presumably built in Memphis because of the large tonnage of cottonseed hulls that accumulate in that area. Although this plant at first used cottonseed hulls, it later had to use corncobs and rice hulls because of the insufficient quantity of cottonseed hulls available for this purpose.

Brownlee,[49] of Quaker Oats Company, was recently granted a patent which describes a digester that is operated continuously. In this process, the hull–dilute sulfuric acid mixture is fed continuously into a horizontal reactor. The hulls and acid are slowly moved along the vessel towards the discharge end by means of a screw conveyor. Live steam at 60 p.s.i. pressure enters near the discharge end of the reactor, passes countercurrent to the hulls, and leaves the vessel near the point at which the hulls enter. With a steam to hull ratio of 1 to 1, a furfural yield of 10% of the hulls charged is claimed. With a steam to hull ratio of 3 to 1, the yield is 14%. The former ratio requires 10 pounds of steam per pound of furfural, whereas the latter requires 21 pounds of steam per pound of furfural. At 60 p.s.i. steam pressure, five to six hours is required for the furfural production operation. At 125 pounds p.s.i. steam pressure, this reaction time may be reduced to about two hours. The furfural–water azeotrope is distilled from the steam–furfural mixture obtained from the reactor. The furfural–water azeotrope contains about 16% water and 0.15% acetic

[44] R. Katzen, A. O. Reynolds, and D. F. Othmer, *Pacific Plastics,* **20,** 91–97 (Oct., 1942).
[45] Northwestern Wood Utilization Council, New Haven, Conn., Bull. No. 7 (1945).
[46] I. A. Pearl, *J. Am. Chem. Soc.,* **64,** 1429–1431 (1942).
[47] F. N. Peters, *Ind. Eng. Chem.,* **28,** 755–759 (1936).
[48] Chem. and Met. Flowsheet, *Chem. & Met. Eng.,* **52,** 132 (1945).
[49] H. J. Brownlee (to Quaker Oats Co.), U.S. Pat. 1,919,878 (1933).

acid. The furfural in this mixture is dehydrated and distilled to produce the pure compound.

Only a few references are found in the literature describing the preparation of furfural directly from cottonseed hulls. Zakoshchikov *et al.*[50] report yields of 15% furfural from cottonseed hulls, and up to 20% furfural from hull bran. They state that the presence of tannins causes lower yields of furfural. Washing of the hulls with water or removal of the lignin by chlorination prior to furfural production gave increased yields.

Furfural can also be prepared from cottonseed hulls by first hydrolyzing the pentosans to xylose and then converting the xylose to furfural. Hurd and Isenhour [51] made a rather complete study of the production of furfural from xylose. They report that hydrochloric acid is about twice as effective as sulfuric acid in this reaction. Fulmer and co-workers [52] investigated the production of furfural from xylose, using hydrochloric acid–sodium chloride solutions. According to their method, the xylose–acid–salt solution is mixed with toluene and refluxed for several hours. The furfural preferentially goes to the toluene layer. It was found that the yield of furfural was dependent only upon the *p*H of the solution for specified concentrations of xylose. The maximum furfural yield of 60% of the theoretical was obtained under several different sets of conditions which ranged from 0.5 *N* hydrochloric acid and 45% sodium chloride with a reflux time of eight hours, to 2 *N* hydrochloric acid and 25% sodium chloride for a reflux time of two hours.

7. Continuous Saccharification

The foregoing information indicates that crystalline xylose, furfural, dextrose, and lignin can all be produced from cottonseed hulls. This possibility enhances the value of cottonseed hulls as a raw material for the saccharification process. Dunning and Lathrop [3] have described a continuous process for the saccharification of cottonseed hulls and other agricultural residues, which involves a two-stage operation. The pentosans are first hydrolyzed by dilute sulfuric acid to xylose. The cellulose is then saccharified by a new concentrated sulfuric acid method which requires much less acid than previous concentrated acid processes. The lignin remains as an insoluble residue. The methods employed permit almost quantitative separation of pentosans and cellulose. The pentosan hydrolysis yields a 15 to 20% xylose solution. The cellulose hydrolysis yields a 10 to 12% dextrose solution.

According to this process, one ton of cottonseed hulls yields 101 pounds

[50] A. P. Zakoshchikov, V. T. Ivanova, and A. M. Kurennova, *Trest Khlopkochistitel. Prom.* (Cotton Ind. Trust), **1,** 87–102 (1933); *Chem. Abst.*, **28,** 5267, 1934.

[51] C. D. Hurd and L. L. Isenhour, *J. Am. Chem. Soc.*, **54,** 317–330 (1932).

[52] E. I. Fulmer, L. M. Christensen, R. M. Hixon, and R. L. Foster, *J. Phys. Chem.*, **40,** 133–141 (1936).

of 93% pure crystalline xylose, 160 pounds of furfural, 680 pounds of dextrose which may be readily fermented by yeast to 42 gallons of 95% alcohol, and 332 pounds of lignin. Assuming a selling price of 5 cents per pound for xylose, 9 cents per pound for furfural, 22 cents a gallon for alcohol, and $3.50 a ton for lignin as fuel, the products from one ton of cottonseed hulls would sell for $29.27.

Based on experimental results from a large-scale laboratory operation and on known data from unit operations, Dunning and Lathrop estimate the cost of producing the above products from one ton of cottonseed hulls to be approximately $21, with cottonseed hulls at $6 per ton. This estimated cost subtracted from the sale value of products leaves $8.27 per ton for sales expense, administration, and profit.

8. Destructive Distillation

Cottonseed hulls, when heated to approximately 650° F. in the absence of air, yield mainly acetic acid, methanol, charcoal, tars, tar oils, creosotic derivatives, and gas. This operation is called destructive distillation.

(a) Methods and Yields of Products. Randolph *et al.*[53] state that the recovery of acetic acid from the destructive distillation of cottonseed hulls is sufficiently high to make the process commercially attractive. They found that the tar from the process is hard drying, unusually resistant to solvents, and high in phenol content.

Nagin [54] has found that the yields of acetic acid and methanol from cottonseed hulls are considerably lower than the yields of these same compounds from birch shavings and sunflower seed. He concludes, therefore, that cottonseed hulls are not the most suitable raw material for the destructive distillation process.

TABLE 218

Yields of Products from the Destructive Distillation of Different Materials[a]

Material	Yield from raw material, %				
	Liquor	Charcoal	Acetic acid	Methanol	Acetone
Rice hulls	40.9	38.44	2.99	2.07	0.41
Low-temperature	43.2	39.80	3.58	1.30	0.62
High-temperature	41.2	37.10	3.17	1.30	0.81
Cottonseed hulls	40.2	20.62	3.75	1.31	0.64
Hardwood planer cuttings (as control)	67.0	18.70	6.67	1.52	—

[a] P. B. Jacobs, *Ind. Eng. Chem.*, **32,** 214–226 (1940).

[53] E. E. Randolph, C. S. Grove, and R. C. Tucker, *J. Elisha Mitchell Sci. Soc.*, **48,** 26 (1932).

[54] K. Nagin, *Masloboino Zhirovoe Delo,* **9,** No. 6, 15–17, 1933; **9,** No. 7, 16–19 (1933); **9,** No. 8, 11–15 (1933); *Chem. Abst.*, **28,** 7571, 1934.

Jacobs [55] has discussed the development of the continuous feed destructive distillation process as applied to agricultural residues. He outlines the methods of operation of continuous feed retorts and offers suggestions relative to their future design. The data in Table 218, which are reported by Jacobs, indicate that the yield of products from the destructive distillation of rice hulls and cottonseed hulls are quite similar, but lower than the yield of products from hardwood planer cuttings. The following statement is made by Jacobs:

"From a commercial standpoint, the process of destructive distillation has been of diminishing importance in recent years. Destructive distillation is a drastic chemical process, tending to bring about complete decomposition into gas and coke, with no by-product recovery. Even if properly controlled, the net yields of usable products are usually comparatively low, and the liquid organic products recovered are complex mixtures frequently difficult to purify. Originally the process was a basic industry, and hardwood served as the principal raw material; but the production of methanol, acetic acid, and recently of acetone by synthetic processes, the substitution of coke iron processes for former charcoal iron, and a tendency toward higher wood costs have combined gradually to restrict the wood distillation business. It has receded from its former prominent position and exists today largely as a by-product industry in connection with blast furnace or lumber operations."

(b) Activated Carbons. McElhinney and co-workers [56] developed a process for the production of activated carbon from the charcoals remaining after the destructive distillation of agricultural residues. They state that activated carbons produced from some residues, particularly oat hulls, pecan shells, and corncobs, were equal and in some cases superior to the activated carbons now on the market.

McElhinney employed the steam activation method of Chaney [57] for the production of activated carbons from agricultural residue charcoals. He developed a continuous feed method for this activation which consisted in conveying the charcoal through a steel tube which was mounted in a brick-lined furnace. The conveyor was turned at such a rate that the charcoal required thirty minutes for passage through the tube. Temperatures of about 950° C. and a steam consumption of 6 to 10 pounds per pound of carbon were employed.

McElhinney estimated the cost of producing activated carbon from agricultural residues, using pecan shells as an example. In this estimation, he assumed that a 27% yield of primary charcoal would be obtained from the destructive distillation process and that the cost of the shells f.o.b. the distillation plant would be $2.25 per ton. He assumed further that the

[55] P. B. Jacobs, *Ind. Eng. Chem.*, **32,** 214–226 (1940).
[56] T. R. McElhinney, B. M. Becker, and P. B. Jacobs, *Iowa State Coll. J. Sci.*, **16,** 227–239 (1942).
[57] N. K. Chaney, *Trans. Am. Electrochem. Soc.*, **36,** 1–91 (1919).

cost of producing the primary charcoal by destructive distillation would be offset by the sale of the condensable products (acetic acid, methanol, acetone) obtained from the process. Under these conditions, the charcoal would be worth about 0.4 cent per pound. A 50% loss on activation raises the carbon value to 0.8 cent per pound. Assuming an additional activation cost of 0.5 cent per pound (for labor, steam, and heat), plus 0.7 cent per pound (for overhead, sales, and miscellaneous), a bulk price of 2.0 cents per pound or $40 per ton might be predicted.

In view of the fact that the volatile products as well as the charcoal from the destructive distillation process have a much lower value than formerly, McElhinney states that "the finding of satisfactory markets for the charcoal would be an important factor in establishing destructive distillation as a successful agricultural residues industry." Because of the large tonnage use of activated carbon in municipal water purification for removal of color and taste (in solvent recovery, gas recovery, and in air purification), it is probable that a market may be developed for the charcoal in the form of activated carbon.

Musser [58] suggests a method for the preparation of activated carbon from cottonseed hull bran. In this method, the bran is carbonized at a temperature of 600° to 650° C. The carbonization requires four hours at the optimum temperature. The charcoal thus obtained is activated at a temperature of 950° C. by means of superheated steam. Musser found that the activated carbon prepared in the above manner is of excellent quality for water purification and is entirely suitable for medicinal uses, after an acid wash.

Basore and Schweickhardt [59] described a high-grade decolorizing carbon which they produced from cottonseed hulls after removal of the pentosans by acid hydrolysis. Their process consisted in heating the extracted hulls at 982° C. in admixture with lime, which reduces the quantity of gases absorbed by the carbon. After cooling, the lime is dissolved from the carbon with hydrochloric acid. The carbon, after thorough washing with water, is activated at 870° C. in the presence of air. The authors state that the resulting carbon is of high quality and is superior to each of 11 commercial carbons collected from this country and Europe. An analysis of this process indicates that the cost of chemicals, fuel, and water amounts to 1.897 cents per pound of activated carbon. This cost is calculated on the basis of a 16% yield of activated carbon from the hydrolyzed hulls.

There appears to have been no industrial application of these processes for the destructive distillation of agricultural residues or for the production of activated carbon from them.

[58] D. M. Musser and H. C. Engel, *Ind. Eng. Chem.*, **32,** 1636–1638 (1940).
[59] C. A. Basore and W. K. Schweikhardt, *Alabama Polytech. Inst. Eng. Expt. Sta. Bull.*, **2,** 1–29 (1931).

V. Conclusions

It was stated that the primary purpose of this discussion of cottonseed hulls was to ascertain the reasons for their apparent retarded use as an industrial raw material. From the information available, it appears that the price that cottonseed hulls command as a roughage is too high to permit their extensive use in the chemical process industries. For example, the products from one ton of hulls, from the saccharification process described by Dunning and Lathrop,[3] are valued at $29.27. At $6 per ton for hulls the cost of production is estimated at $21, leaving $8.27 for sales expense, administration, and profit. At the average annual price of $8.81 per ton for cottonseed hulls, this $8.27 is reduced to $4.46. At $13.27, the price cottonseed hulls have attained in several different years, the $8.27 for sales expense, administration, and profit is wiped out. At $2.25 per ton for raw material, the activated carbon described by McElhinney,[56] might be produced for $40 per ton. At a price of $8.81 for raw material, the activated carbon increases in cost to $86.60 per ton.

Not only is the average annual price of cottonseed hulls apparently too high for chemical process utilization, but the variation in price from year to year is not at all conducive to such utilization. It is true that there are areas in which the local demand for cottonseed hulls does not consume the supply and that the price of hulls in these areas is lower than the average annual price. The tonnages available in these localities, however, are variable and normally too small to support a large industry. A plant for the production of xylose, furfural, alcohol, and lignin, or for the production of the other chemicals discussed would require preferably 100,000 tons of hulls a year and in no event less than 50,000 tons a year. It must be emphasized that this 50,000 to 100,000 tons of hulls must be available each and every year.

The use of cottonseed hulls in floor sweeping compounds, plastics, bedding materials, and road construction presents a different situation. Relatively small tonnages of hulls would be necessary for these outlets. In some cases, the margin of profit per ton of raw material is greater than in chemical process uses. In addition to cottonseed hulls, there are several other materials that can and are being used for each of these purposes. If the local feeding demand consumes the local supply of hulls, these other materials will be employed.

All the information indicates that the feeding industry is the most remunerative outlet for cottonseed hulls. Normally, 85% of the hull production is consumed by this market. It would be logical, therefore, to expand the local feeding industry in areas of "surplus" hulls as a means of increasing the value of the remaining 15% of hull production.

The economic status of any raw material, however, is subject to change.

In the future, cottonseed hulls may be replaced in, or found unsuitable for, the feeding market. If large tonnages of hulls are then available at $5 or less a ton, they will undoubtedly find a place in the process industries. The process industry or industries that will consume the bulk of the cottonseed hulls will then be an outgrowth of the research and development work now being conducted on hulls and other agricultural residues.

CHAPTER XXIV

COTTON LINTERS

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The use of cotton linters for their fiber properties and as a source of cellulose contributes an average annual return to the cottonseed industry of about thirty million dollars. This represents a production of some 1.2 million bales of cotton linters, which is of considerable magnitude for an industry based on a material originally considered a nuisance to cottonseed processors.

I. Development of Uses for Cotton Linters

A. Earlier History

1. Use as a Fiber Material

At first, cotton linters were removed from the fuzz-covered ginned cottonseed to permit more efficient recovery of the oil. Although the amount removed for this purpose varied in different mills, the product was used in industries where a short cotton fiber could be tolerated. Even the longer cotton linters fibers are too short for spinning into anything but low-grade yarns. However, the removal of cotton fibers up to some seventy pounds per ton of seed will yield a fiber long enough to respond to a carding operation known as "garnetting." By this process a cotton felt or batting can be prepared which is suitable for padding of mattresses, furniture and automobile upholstery, and other similar uses. This use of the longer fibered cotton linters has grown to some 400,000 bales annually.

Other uses based on the fiber properties of cotton linters, either short or long fibered material, have been more varied in their development. Purified and bleached cotton linters are used to some extent in papermaking, as floc for plastics filler and artificial suede, and in the preparation of surgical dressings.

2. Chemical Uses

Another important use of cotton linters is as a source of cellulose for the chemical industry. Early in the present century, the nitrocellulose

industry reached commercial importance. The cellulose sources—linen rags, bleached cotton rovings, tissue paper—were not very satisfactory. Their high cost and limited supply necessitated the search for a source of cellulose of equal purity and lower cost. Cotton linters met these requirements.

World War I accelerated the use of cotton linters in the chemical industry. The enormous quantities of nitrocellulose used in smokeless powder manufacture were prepared from cotton linters cellulose. To meet this need, the oil mills made major installations for increased recovery of the fibers. During this period, the Federal Government requisitioned all production. Cotton linters were recovered at the rate of 150 pounds per ton of seed, and production for the years 1916 to 1918 averaged just under a million bales of cotton linters per season. When this need terminated, consumption dropped enormously, and in the early 1920's the cellulose industry was in the doldrums.[1]

The nitrocellulose lacquer industry developed after the war, and viscose manufacture began to mushroom in the late 'twenties. In the expansion of the chemical cellulose industry, cotton linters played a major role. The economical nitration of cellulose for lacquer required the use of purified cotton linters. After 1935, the reduced cost of nitric acid and development of methods for the production of wood pulp cellulose permitted the latter gradually to displace chemical cotton for the manufacture of lacquer nitrocellulose. In the first years of viscose manufacture, rayon sold at two dollars a pound in competition with five-dollar natural silk. During these years, the higher purity cellulose from cotton linters was used in quantity. However, as the price of viscose rayon was reduced (to fifty cents a pound in 1936), cotton linters cellulose was displaced entirely by wood pulp.

These experiences illustrate a characteristic of the demand for cotton linters in the chemical cellulose industry. The superior cellulose from cotton linters commands first interest in the chemical industry, but its variable and higher cost has promoted parallel use of wood pulp cellulose as well. Under this stimulus, the wood cellulose manufacturers have improved their product steadily to meet the needs of the chemical industry. Only where the properties of the cellulose derivative require the quality of cotton linters cellulose will industry now pay the premium for this chemical cotton pulp.

B. Recent and Present Utilization of Linters

1. Present Demand for Chemical Cotton

The quality of chemical cotton pulp is in demand in high-tenacity rayon and in the cellulose derivative plastics and films. To these products,

[1] From *U.S. Dept. Agr. Circ.*, **No. 175** (1921).

the cellulose from cotton linters contributes strength, clarity, and freedom from color.

Tire cord rayon is made from chemical cotton (purified cotton linters) in order to obtain the superior fatigue strength so necessary in tires, especially those for trucks and busses. Special-strength rayon, made by the acetate process, is obtained from chemical cotton. In the cuprammonium rayon process, in which the production of very fine fibers is a feature of the operation, chemical cotton is used to manufacture the finest deniers,[2] with strength necessary for hosiery and other textiles of gossamer character.

Plastics from cellulose nitrate, cellulose acetate, ethyl cellulose, and other cellulose esters and ethers are made from chemical cotton. The clarity and freedom from color necessary for the crystal and the translucent pastel-colored objects which are in demand are secured through the use of purified cotton linters. The strength of photographic film and sausage casings is obtained by the processing of chemical cotton.

2. Consumption. Foreign Trade

In the years prior to 1939, the consumption of cotton linters in the chemical cellulose field amounted to about 400,000 bales. During World

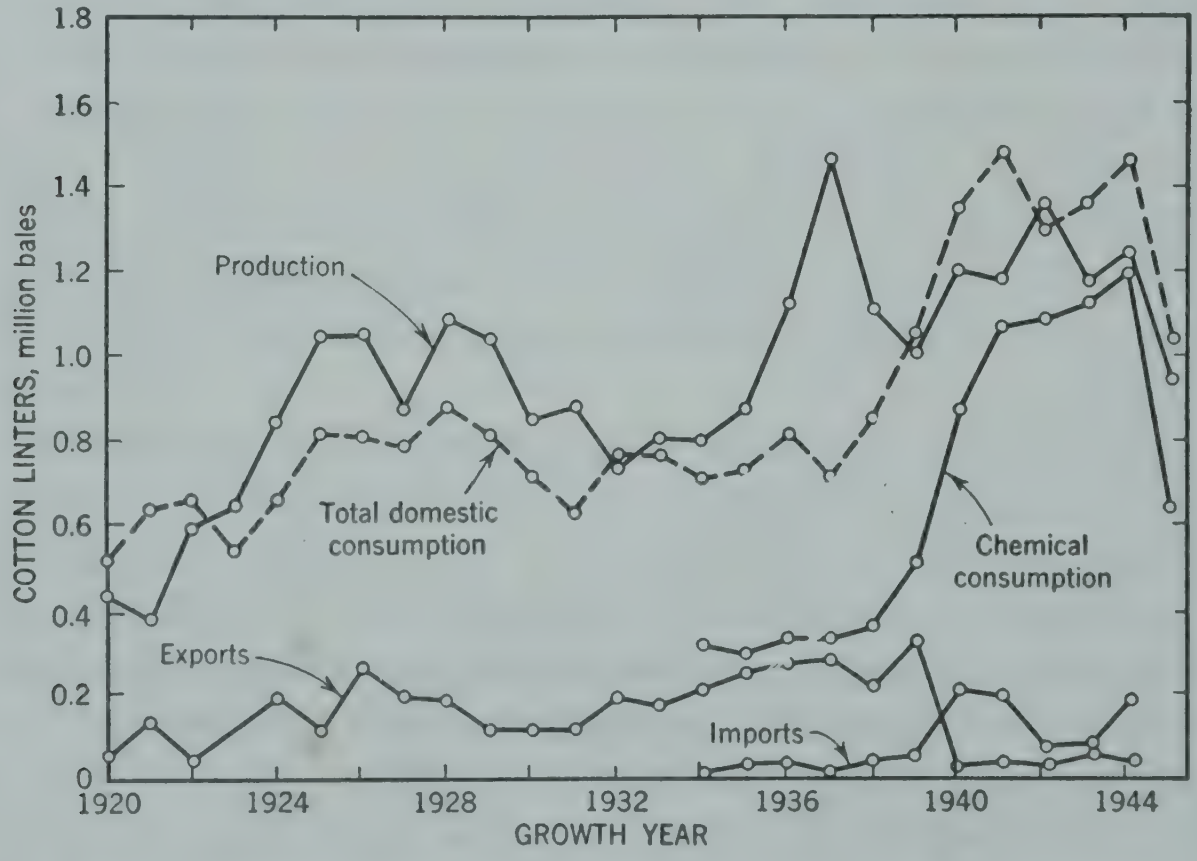


Fig. 204. Cotton linters: United States production, consumption, and foreign trade in recent years. (From publications of the Bureau of the Census and the U.S. Department of Agriculture.)

War II, cotton linters were again vital to war industries and their production and consumption were again controlled by the government. In

[2] Denierage of a yard is the weight in grams of a length of 9,000 meters. Yarn of low denierage is a fine yarn; a high-denier yarn is coarse.

this period, the chemical uses of cotton linters were more diversified than in World War I, with wood pulp sharing the burden for production of smokeless powder nitrocellulose. The curves in Figure 204 trace the recent production and consumption of cotton linters in the United States. The trends in foreign trade are also shown.

Exports of cotton linters in the period just prior to 1940 averaged more than 250,000 bales annually. Much of this material was intended for chemical uses in Europe. The indicated increase in imports of cotton linters resulted from increased production in South America, a shifting of markets in the prewar period, and an increase in demand for the batting grade of cotton linters.

3. Future of Linters Utilization

At present, cotton linters face increased competition in all their fields of use. The development of new padding materials, such as foam rubber, is of interest in the mattress and upholstery fields. Improvements in the properties of wood cellulose will be important in the marketing of purified cotton linters to the chemical industry. Considerable research is being carried out on cotton linters in an effort to maintain and expand its uses in the face of competition.

II. Types and Grades of Linters

By the delinting of ginned cottonseed, cotton linters are recovered as three major types. These are first-cuts, second-cuts, and mill-runs. A small quantity of hull fiber is also recovered from some of the hulls after separa-

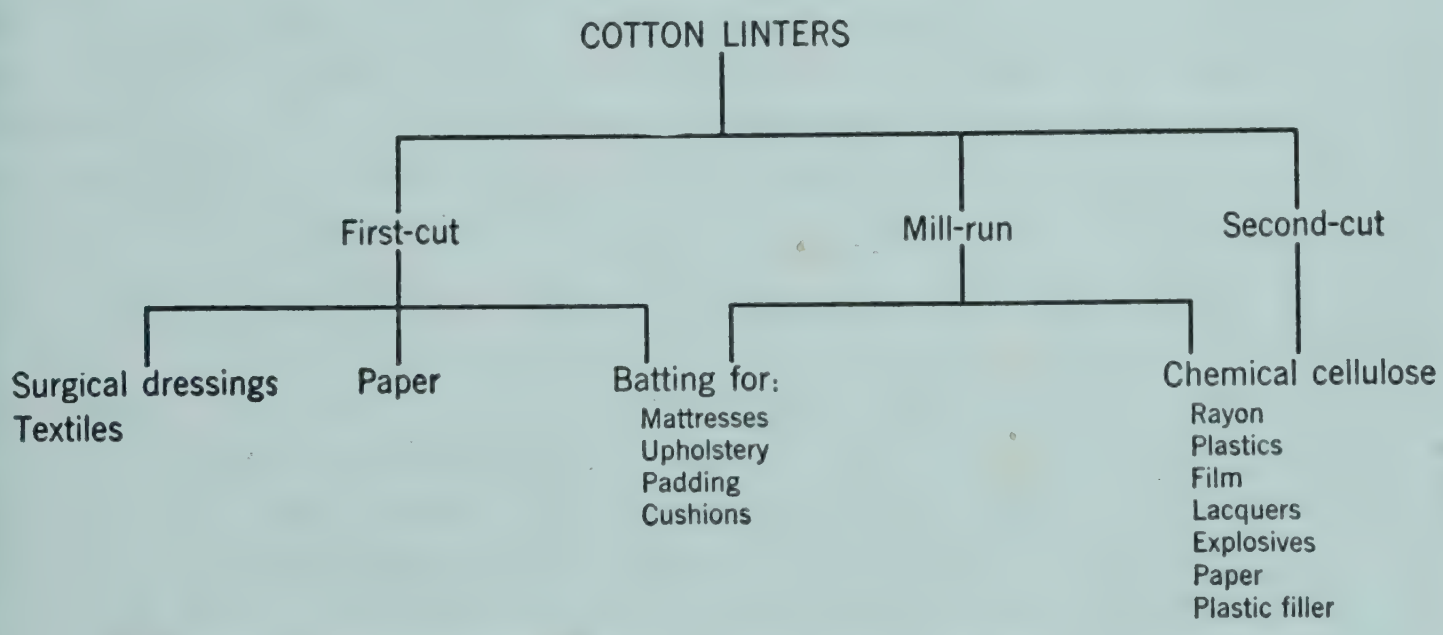


Fig. 205. Industrial utilization of the three types of cotton linters.

tion of the meats. These types of linters and their recovery are discussed in Chapter XIV. It will be recalled that first-cuts and second-cuts are portions removed by passing the seed in two successive steps through the delinting equipment. The first-cuts may amount to 30 to 75 pounds per ton

of seed and the second-cuts will be obtained in such additional amount as to yield a total of 180 to 210 pounds of cotton linters per ton of seed. Mill-run linters are a product of a single delinting of the cottonseed and may range in quantity from about 70 to 200 pounds per ton of seed. The industrial utilization of the three types of cotton linters is shown diagrammatically in Figure 205. In Figure 206 is shown the characteristic distribution of fiber lengths in the three types and in "hull fiber."

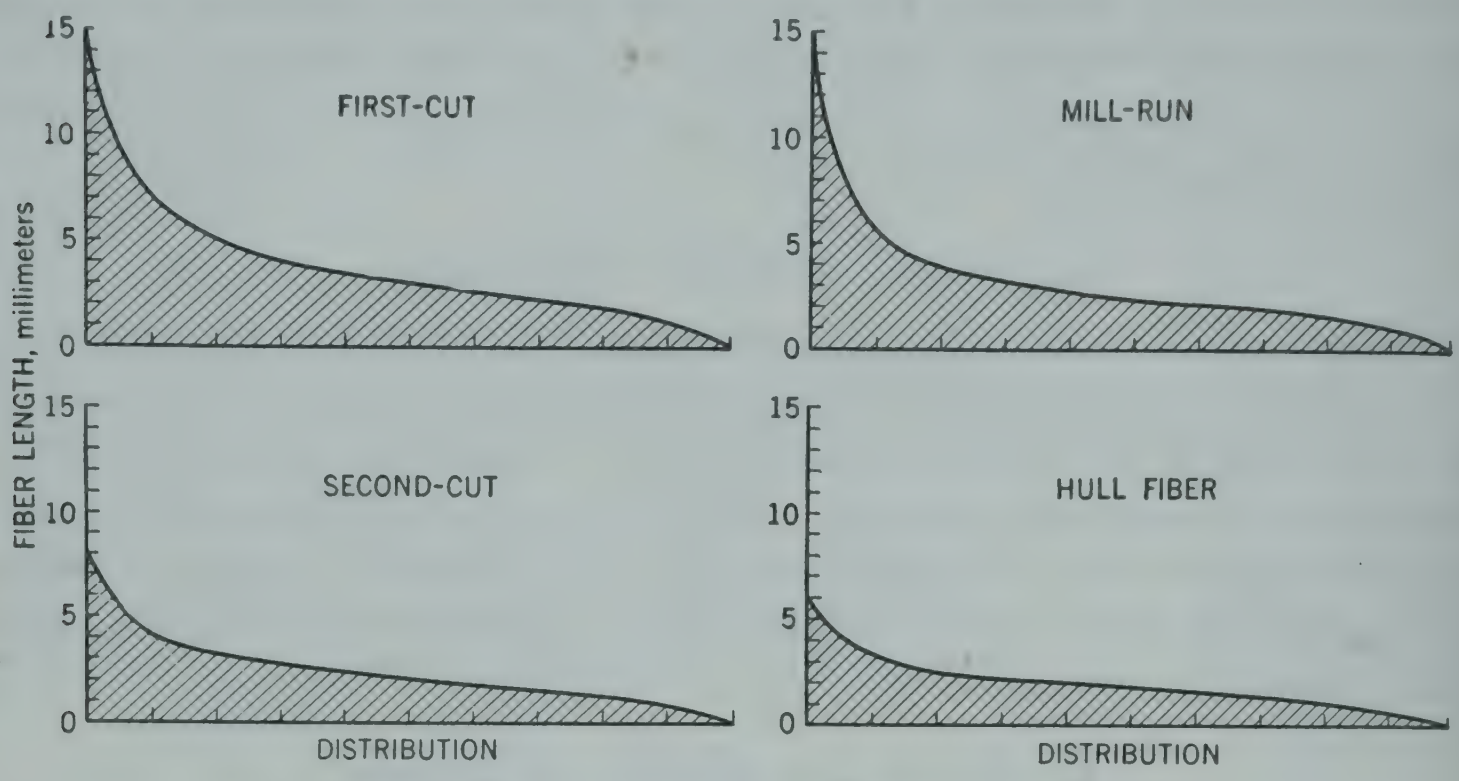


Fig. 206. Distribution of fiber lengths in the different types of cotton linters.

It is recognized that the type of cotton linters (as described above) does not determine the quality of the product for its various uses. For the batting trade, fiber length, resiliency of the batt, yield of batting, and color are important factors. The yield of chemical cotton, kind and amount of foreign matter, and fiber length are critical to the manufacture of cellulose for the chemical industry. Therefore, the United States Department of Agriculture has sponsored the use of standards which were established in 1926.[3] There are seven standard grades, U.S. No. 1 to U.S. No. 7, which are differentiated according to the fiber length and amount of foreign matter. The grades include products of the three different "character" types known as Western, Valley, and Southeastern, and include the color range, buff to olive, to be expected in the particular grade.

In the batting field, the character of the fiber is of great importance. The character is determined by the average fiber length and fiber-length distribution, the resiliency of the mass of fibers, and its degree of smoothness. In the government grades, linters of Western character are relatively short and regular in length, are harsh and resilient, and generally are of a

[3] From *U.S. Dept. Agr. Misc. Pub.*, **No. 242** (1936).

low degree of smoothness. Valley character denotes long average fiber length with irregular fiber-length distribution, and a soft mass structure, with a moderate degree of smoothness. Linters of Southeastern character are of intermediate average length, with good uniformity of fiber length; they form soft masses of fiber with good smoothness. Government-graded linters will show grade number, character, and color.

There is a desire to measure more accurately some of the character elements of linters for the batting trade. Some agencies are developing evaluation tests which will eliminate some of the personal element in the grading of linters. Tests which will accurately measure the quality of the batt made from given lots of cotton linters are the desired goal of the suppliers.

Government grading emphasizes the properties of linters for the manufacture of batting, this being the major market when this grading system was established. The properties desirable for chemical cellulose manufacture are not covered too well by this grading system. For chemical use, a specialized grading is generally resorted to by the buyers; cotton linters are bought on the basis of yield and quality grading. Yield of cellulose is determined by the Cellulose Yield Method, an official method of the American Oil Chemists' Society. Samples representing the lot for purchase are analyzed in a suitably equipped laboratory by the standard test procedure. This yield forms the basis for determining price. The price schedule is based on a cellulose yield of 73%, with adjustment made for variations from this base. The yield of cellulose however, does not solely determine the value of the product for chemical purposes. There can be present in cotton linters various amounts and kinds of contaminants which respond differently to the purification treatments. Portions of the inner lining of the boll, cottonseed hull particles, stems, etc. are particularly objectionable. Some do not respond to purification; others leave undesirable residues in the finished cotton cellulose. The effects of such contamination are out of all proportion to the weight of these materials. Direct methods of measuring the contaminants in the cotton linters have been attempted.[4] However, the best evaluation is still the small-scale complete purification of the cotton linters sample and its conversion to a critical cellulose derivative like cellulose acetate. The comparison of the quality of the chemical cotton and its cellulose derivative to the properties of the original linters has allowed the development of a skill in judging the quality of cotton linters for chemical cotton on the basis of physical inspection.

Neither field trash nor boll lining in cotton linters can be successfully removed in purification. Their effect can only be minimized by blending to yield an inferior though tolerable product for less critical uses. Hulls,

[4] T. L. Rettger, *Oil & Soap,* **22,** 7–10 (1945).

as particles of the seed coat are known, will disintegrate more or less, depending upon their size and the conditions of purification. However, dispersed portions of the palisade wall will be left in the chemical cotton (see Chapter III). These residues interfere in the preparation of cellulose derivatives which are to have good filtration properties, and are free of haze in solution, film, or plastic.

The grading of cotton linters for chemical cellulose is not standardized among the suppliers and buyers. Sales are made by agreement on individual lots after inspection of the materials.

III. Production of Cotton Batting Employing Cotton Linters

For the preparation of cotton batting for mattresses and upholstery, the fibers are carded in a garnett machine. This device works the fibers into a thin uniform web at the rate of 300–500 pounds per hour. The web is built up into a thick pile to form the batting. Generally, this pile is built up on a slow-moving apron, and from one to eight garnetts may be feeding their web to the accumulating pile as it moves along. The apron speed is determined by the amounts of garnetted fibers being fed to the apron and the thickness or weight of pad desired. The pad is passed through press rolls and rolled or cut into individual pads of desired size.

To obtain batting with the properties desired for upholstery or mattress padding, it is necessary to select and combine several fibers. Some of these fibers will be the longer fibered first-cut and mill-run linters together with staple cotton fibers obtained as a waste from textile operations or purchased as such on the market. The selection is made up to give a high yield of uniformly resilient padding.

Before the selected fibers can be garnetted into batting, the bales must be opened and the fibers loosened, cleaned, and mixed. The equipment for this is generally designed to handle all the fibers to be used in the line of garnetts. Therefore, the capacities may vary from about 400–4,000 pounds per hour. Equipment for the larger capacity will usually include a bale breaker, a picker, and a willow. For smaller capacities, the bales may be opened and fed manually to a willow for loosening the fibers, mixing, and cleaning.

The willowed mixture is delivered to the garnetting area by an air system of the suction type. The fibers are collected on a suction condenser which also aids in the removal of fine dust. The fiber mixture is delivered to the hoppers of each garnett feed. Here, the fibers are accurately weighed so that a predetermined quantity per unit area will be delivered to the feed belt. They are then fed to a preliminary set of rolls in the garnett. A rapidly revolving cylinder dressed with a metal-toothed wire pulls the fibers onto the roll as a thin film. Around this cylinder is placed a series of pairs of toothed rolls called workers and strippers. These work

over and smooth out the rough, tangled, and lumpy mass of fibers on the cylinder. The partially carded stock is raised and removed by a doffing roll to be fed to a finishing set of rolls. Like the preliminary set, this too consists of a cylinder with its series of cooperating worker and stripper rolls. On this finishing set, the final carding is completed. To remove the maximum amount of the carded fibers, modern garnetts are equipped with two sets of doffing rolls. These remove two fibrous webs from the face of the final cylinder and combine them at the lapping machine, which moves back and forth to deposit the carded web in a pile on an apron of the machine. The lapper is operated to yield a batt of the desired weight for upholstery or mattress use [5] (see Fig. 207). The finished batt is trimmed to the desired width or widths and rolled onto a spool or cut off to form pads of desired size. In the latter case, the pad is often folded automatically in thirds to permit easy handling. The rolled padding or folded batt is then ready for use in the manufacture of mattresses or upholstery.

IV. Production of Chemical Cotton

The use of cotton linters permits the production of chemical cellulose of high α-cellulose content and of high viscosity.[6] In the manufacture of the chemical cotton there is retained in the cellulose a narrow distribution of molecular sizes and a structure favorable to the manufacture of strong rayons, films, and plastics from its derivatives. The high purity and excellent color of chemical cotton as obtained from cotton linters are also desirable features in chemical manufacture.

This superior cellulose is obtained from a selected supply of second-cut linters, mill-run linters, and/or hull fiber. These shorter fibers are preferred for their economy and ease in processing; they also yield superior cellulose. The mixture is prepared mechanically for digestion in mild alkaline liquors, and the digested cellulose is bleached in multistage operations with thorough washing between the several steps. The product may be dried in the loose fibrous condition or converted to a sheet and dried on a paper machine. The products are made to the exact specifications of the manufacturer of cellulose derivatives and the various operations in the purification of the cotton linters are carefully controlled.[7–10] A flow sheet of operations is shown in Figure 208 on page 903.

[5] T. W. Allen, W. F. Bokum, and J. H. Senior (to Proctor & Schwartz, Inc.), U.S. Pat. 1,833,811 (1931).

[6] The viscosity of cellulose, as determined in standardized cuprammonium solution, is a measure of the average molecular size of the cellulose.

[7] W. D. Munson, *Ind. Eng. Chem.*, **22,** 467–471 (1930).

[8] J. A. Lee, *Chem. & Met. Eng.*, **48,** No. 4, 90–91 (1941).

[9] *Chem. & Met. Eng.*, **48,** No. 4, 108–111 (1941).

[10] E. F. Hinner, in E. Ott, ed., *Cellulose and Cellulose Derivatives,* Interscience, New York, 1943, pp. 519–533.

A. Preparation of Raw Linters before Purification

Cotton linters previously graded by physical inspection at the oil mill are further evaluated and segregated when received at the linters purification plant. The carload lots are sampled and tagged, and the samples are subjected to a complete laboratory-scale purification. The chemical cotton from the sample is analyzed for its chemical and physical properties and the lot of cotton linters is graded thereby for its quality characteristics.

In the preparation of a specific grade of chemical cotton, bales of suitable cotton linters are opened and worked into a fluffy condition by bale opening machines and mechanical pickers. The fluffy linters are then conveyed in an air stream to the digestion area. Advantage is taken of this air-borne condition of the linters to effect a separation of heavy contaminants.

B. Digestion

In the digestion of cotton linters, the maximum removal of noncellulosic material is carried out while effecting adjustment of the viscosity of the cellulose to the desired level. The fat, waxes, proteins, coloring matter, pectic substances, and inorganic matter are solubilized. Chemical attack of particles of the whole seed coat (hull) is made as effective as possible. The epidermis of the seed coat, which is present in considerable amount in most linters, is removed in the digestion and subsequent washing. In all, about twenty-five per cent of the original linters is removed in digestion.

The concentration of alkali, the temperature of digestion, and the time of digestion determine the degree of purification achieved—and the amount by which the viscosity of the cellulose is reduced. The addition of small amounts of soaps or other detergents aids in removing some of the undesirable materials, such as waxes.

Commercial digestion of cotton linters is generally carried out in mild alkali solutions containing 2.5 to 3.5% sodium hydroxide. The temperature may range from 275° to 340° F. (about 30 to 100 p.s.i. steam pressure), and the cooking will be completed in two to six hours. The digesters may be of the vertical stationary or horizontal rotary type. The charge of about seven thousand pounds of linters is well mixed with accurately prepared caustic solution in the ratio of ten parts of liquor to one part linters. The temperature and time needed for digestion depend upon the grade of chemical cotton in preparation. At the end of the digestion period, the charge is blown from the digester. A cyclone separator recovers the stock, which drops to a wash tank. About 75,000 gallons of water will be used in thoroughly washing the stock free of all digestion liquor.

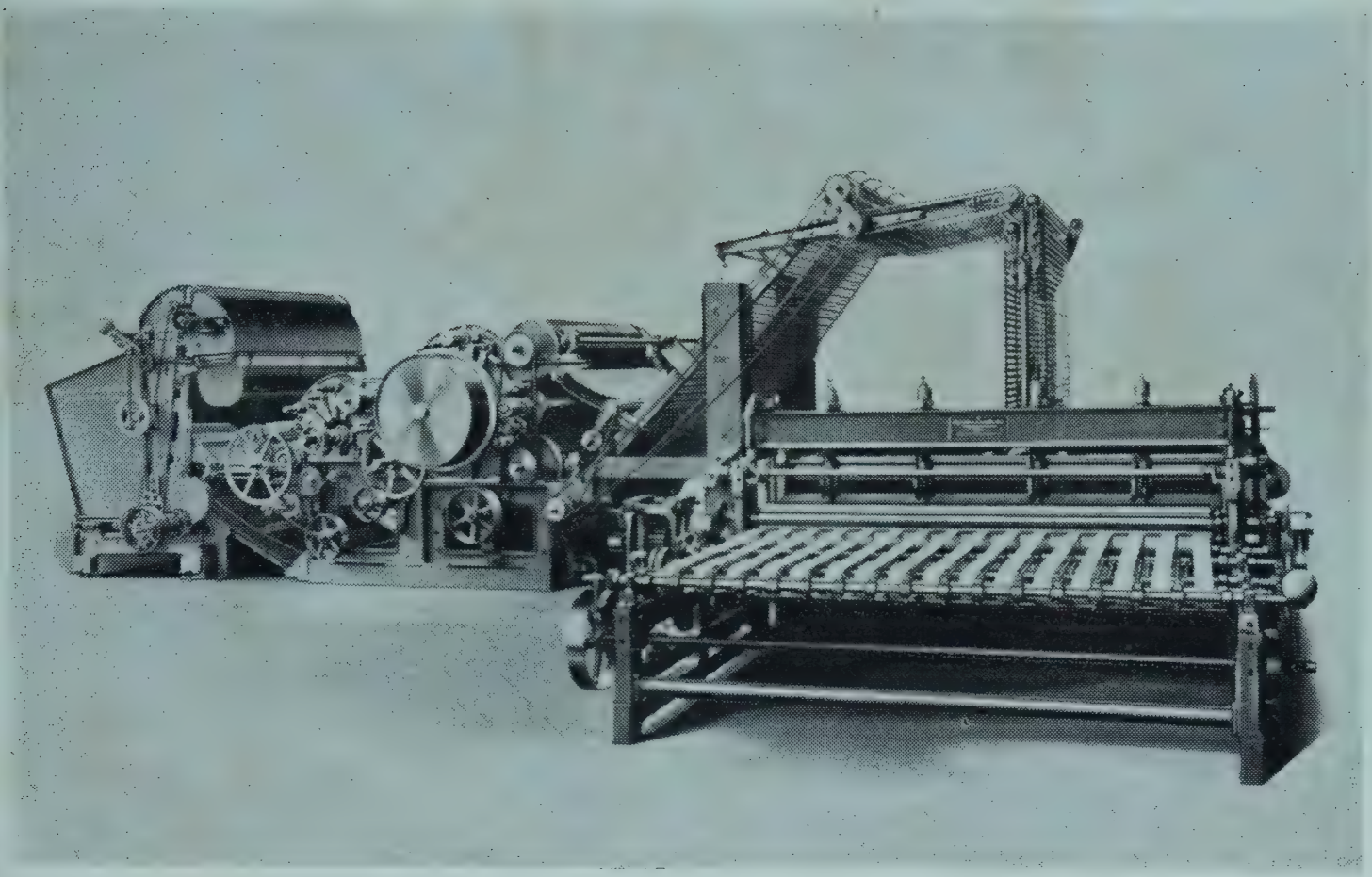


Fig. 207. Garnett machine for preparing batting from cotton fibers. (Courtesy *Proctor & Schwartz, Inc.*)

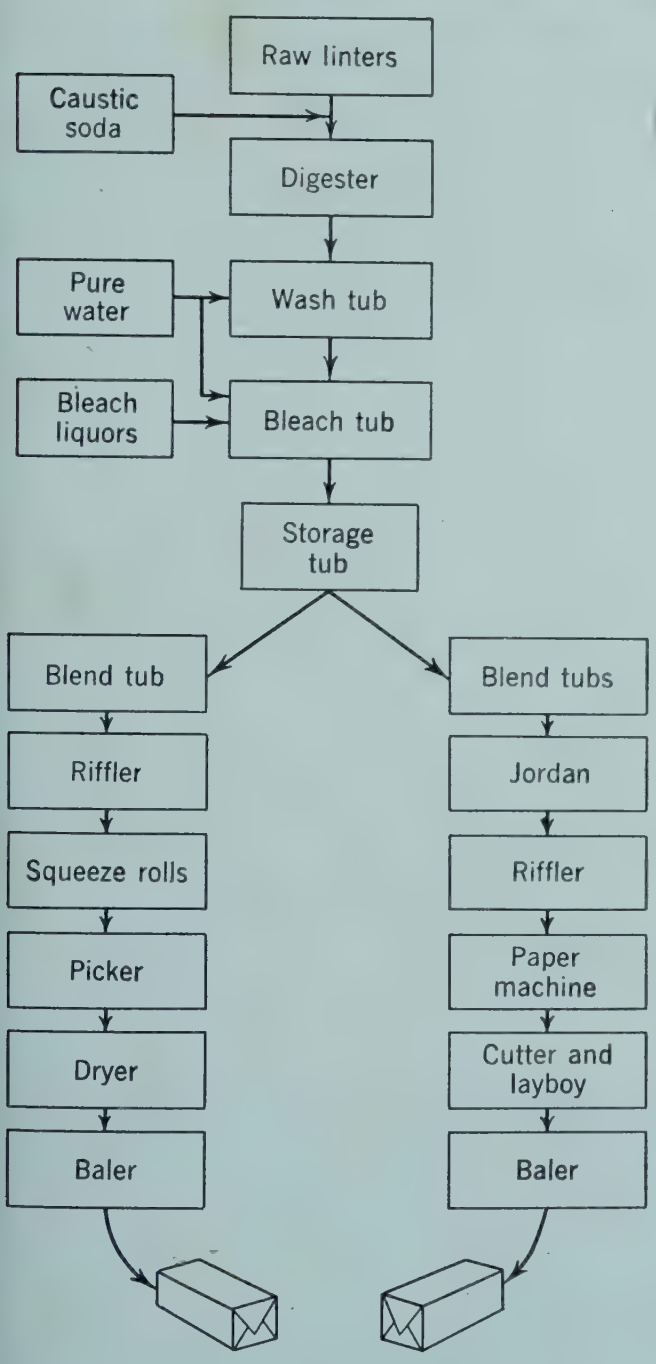


Fig. 208. Manufacture of chemical cotton from cotton linters.

C. Bleaching

The digested and washed cotton linters are now free of most of the undesired material except color bodies. Color is removed by bleaching with one or another of several bleaching agents. Generally, chlorine and hypochlorite liquors are used, but chlorous acid, peroxides, permanganates, or similar agents may be employed. In bleaching, the viscosity of the cellulose is also affected; hence, conditions are selected to balance color improvement and viscosity reduction to the desired levels. The factors considered in obtaining the desired balance are *p*H, concentration of reagent, temperature, and time of bleaching.[11]

[11] L. M. Sheldon (to Cellulose Research Corp.), U.S. Pat. 2,190,274 (1940).

The color bodies to be removed from digested cotton linters have a low bleach demand. However, multistage bleaching may be used to advantage to effect the best bleaching treatment. These operations are carefully controlled and adjusted for each of the different types of chemical cellulose.

Sodium or calcium hypochlorite is the most frequently used bleaching agent for chemical cotton. Adjustment of *p*H is made with sulfuric acid or sodium hydroxide. Operations are generally carried out at low stock densities in large well-agitated tubs constructed of special alloy steel. Each bleach step is followed with a thorough washing.

The recovered chemical cellulose is analyzed at the various bleach stages and should fall within a narrow range of chemical properties. In order to supply continuously lots of chemical cellulose of uniform chemical and physical properties, the finished batches of cellulose are blended as a slurry in ten- to fifteen-ton lots.

D. Drying Chemical Cotton

The finished chemical cotton may be dried in loose or in sheet form. The drying operations are carried out under conditions to retain the best physical form and reactivity for its ultimate use. Chemical cotton in loose form is used in the manufacture of cellulose nitrate, cellulose acetate, and paper. Sheeted chemical cotton is employed in viscose and cuprammonium rayon manufacture and in the preparation of ethyl cellulose, carboxymethylcellulose, and paper.

On the way to the drying operation, the dilute slurry is riffled to remove heavy suspended matter, such as sand, which may have remained in the pulp. At the loose pulp dryers, the stock is thickened and reduced to a moisture level of about 50% by rubber squeeze rolls. The damp cotton is opened to a fluffy form in high-speed pickers and discharged onto the apron of a tunnel dryer.

The tunnel dryer is a continuous device which conveys the chemical cotton through a countercurrent stream of heated air. To obtain the desired properties in the cotton, this air is carefully controlled in temperature and volume. In the production of acetate grades, for example, low-temperature drying is generally employed. Most types of finished chemical cotton have a maximum moisture content of 7%.

The dried cellulose is passed over a magnetic separator and is then baled, weighed, and stored until analysis of the cellulose is completed before shipment. The bales have an average weight of 145 pounds per bale.

For preparing chemical cotton in sheeted form, the slurry of stock at low consistency is reduced in fiber length and made smooth in flow by jordaning. The product is then formed into sheets of desirable structure on a Fourdrinier paper machine. The wet web of paper is carefully dried

in such a manner as to cause it to retain the properties desired for chemical use. The sheet is generally of a standard thickness of 0.040 inch and of a density of about 0.4 g. per cc. The finished cellulose is cut to sheets of specified dimensions and packaged in units of 200 pounds, or it may be packaged in rolls. These packages are weighed and wrapped in kraft paper for shipment after analyses are completed.

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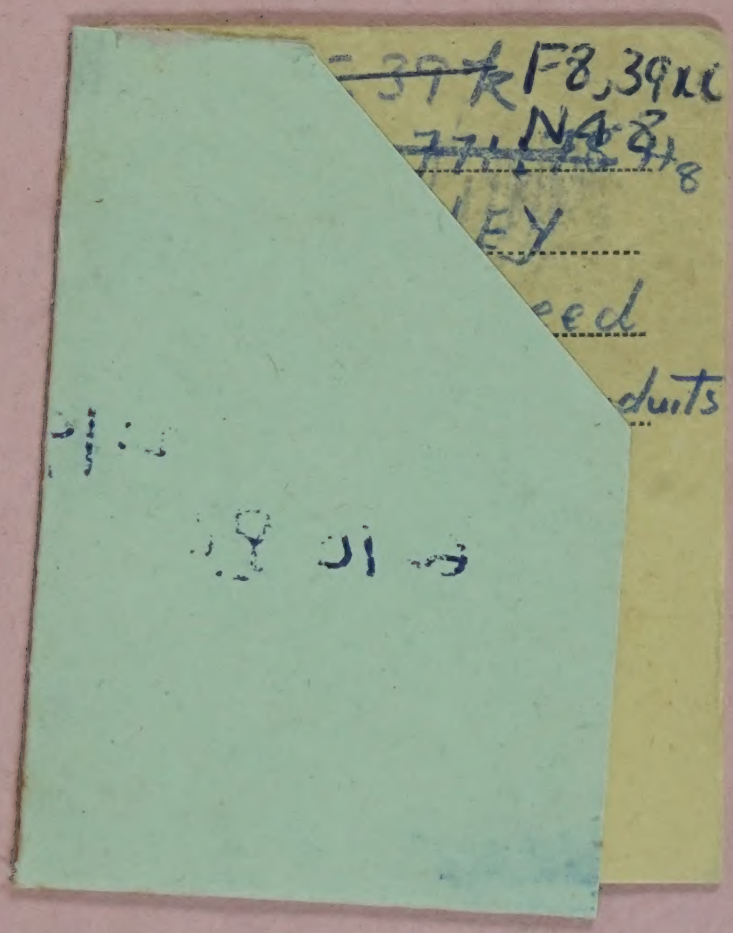
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